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# Elemental Matters

## AN INTRODUCTION TO CHEMISTRY

**Professor Deborah G. Sauder**  
**Georgia Gwinnett College**

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## **An Introduction to Chemistry**

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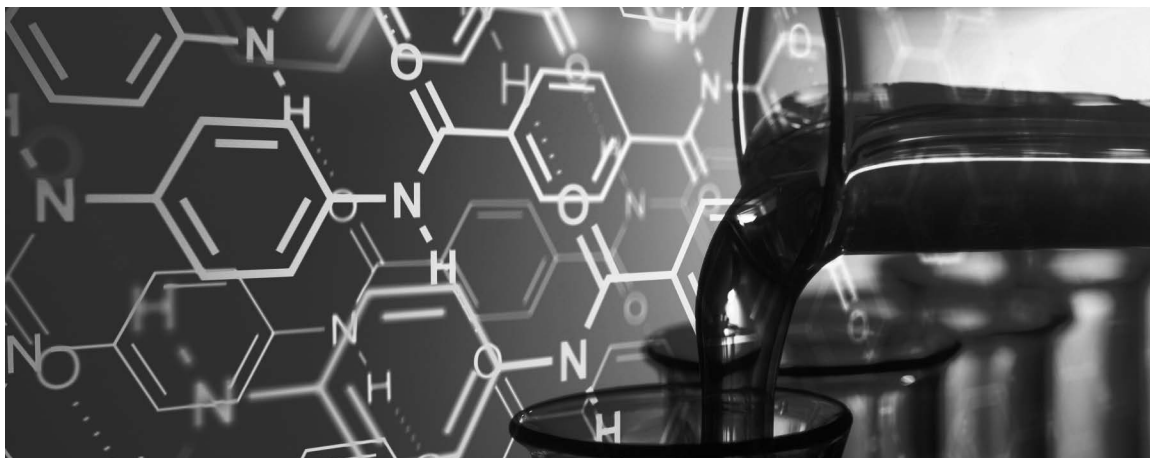
## About Your Professor

### Deborah G. Sauder

Deborah G. Sauder is an associate professor of chemistry at Georgia Gwinnett College in Lawrenceville, Georgia. She completed her Ph.D. in physical chemistry at Johns Hopkins University in 1991, followed by two years as a National Research Council postdoctoral research associate in the Molecular Physics Division at the National Institute of Standards and Technology in Gaithersburg, Maryland. She was soon after appointed to the faculty at Hood College in Frederick, Maryland.

Professor Sauder became involved in pedagogical reform efforts in the mid-1990s. She was an active participant in the Middle Atlantic Discovery Chemistry Project (MADCP), where she developed strategies to improve general chemistry student understanding of bond strength and of basic thermodynamics. As an outgrowth of these efforts, and under the leadership of Dr. Sharon Smith, emeritus professor of chemistry at Hood, she coauthored (with Kathryn Henry Smith and Karen Borgsmiller) Hood's "Experience Chemistry!" curriculum currently available from Pearson Custom Publishing. The curriculum was designed to promote conceptual understanding of basic chemistry in a diverse student body. It employs an integrated lab-lecture format and extensive use of hands-on activities. She was named a Project Kaleidoscope (Association of American Colleges and Universities) "Faculty for the Twenty-first Century" in 1997. Sauder was a founding member of the Physical Chemistry On-line (PCOL) consortium. The seven founding faculty members of PCOL shared the Gustav Ohaus Award for Innovation in College Science Teaching from the National Association of Science Teachers in 1999.

Dr. Sauder joined the Georgia Gwinnett College faculty in 2006. She is active in several professional organizations and most recently served as chair of the Georgia section of the American Chemical Society and as 2010 cochair of the Atlanta regional Project Kaleidoscope group.



## Introduction

The study of chemistry may have truly begun when early humans started mixing organic and inorganic materials purposefully and, many times, by lucky accident. When they didn't harm themselves or cause their own deaths, they often discovered that their experiments were beneficial. As time passed and experimentation continued, the properties of different materials were written down to be passed on to future generations.

Shamans, healers, and alchemists became mainstays of clans, tribes, and larger populations as the power of different combinations of materials was uncovered and used. By the time of the ancient Greeks, many of the basics of what modern humans call chemistry were known in practice, but mostly in folklore and myth. Progress was hampered by inappropriate models of why chemicals behaved the way they did, supporting the random and magical interpretation of their behavior.

Around the seventeenth century, practitioners of chemistry began scientific chemical investigations using newer technologies and a better understanding of physics and mathematics. Fundamental changes in the conceptual models of chemical behavior that researchers employed allowed a much more systematic evaluation of familiar processes and transformations. The systematic approach of the scientific method supported the industrial revolutions of the eighteenth and nineteenth centuries and continues to enhance technology into the modern era with the development of synthetics and nanotechnologies.

Our modern civilization simply would not be possible without the chemical compounds and the diverse uses of chemistry. As amazing and useful as chemistry is, it can be as hazardous to society as helpful. Scientists today employ an increasingly sophisticated understanding of chemistry to create more from what is available and known, while ensuring that new products and future uses are reliable, energy efficient, and safe.

## Lecture 1

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### Water: A Natural Wonder

The Suggested Readings for this lecture are the American Chemical Society and Jerry A. Bell's *Chemistry: A General Chemistry Project of the American Chemical Society*, chapter 1: "Water: A Natural Wonder," and Linus Pauling's *General Chemistry*.

All living systems are composed primarily of water ( $\text{H}_2\text{O}$ ), and 70 percent of the Earth's surface is covered with water and aqueous solutions. You already know a lot about water. You are familiar with it as a solid, a liquid, and a gas. Chemists call these the *phases of matter*. You probably also know that water transitions from one phase to another at specific temperatures;  $32^\circ\text{F}$  or  $0^\circ\text{C}$  is the melting, or freezing point, of water, depending on whether you start with the solid or liquid. The boiling or condensation point of water is  $212^\circ\text{F}$  or  $100^\circ\text{C}$ .

You are familiar with the macroscopic, or visible, differences between solid, liquid, and gas phase water. Solid water—ice, snow, hail—has a definite volume and a shape unrelated to that of any container in which you put it. Liquid water forms drops when present independently in small amounts. Although its volume is independent of its container, its shape conforms to that of its container when more than drops are present. Gas phase water is invisible. Most of the gas phase water we encounter is distributed in air. Although water vapor is invisible, we feel it, and most of us are sensitive to high humidity.

When chemists discuss the properties of water, they are considering pure water. Outside of the lab, however, we rarely encounter chemically pure water. Rainwater contains dissolved gases and dust from our atmosphere. Pure spring water contains dissolved salts from geologic formations. Here the word *salt* is used in the chemical sense to describe a wide variety of inorganic compounds that dissolve in water. The water from your tap contains trace amounts of fluoride salts, and other salts and chemicals. The closest you can come to pure water is water purified by reverse osmosis or distillation. This is water you can buy by the gallon at most grocery stores. Both distillation and reverse osmosis are techniques that allow the chemical components naturally present in water to be separated from the water itself.

If you have ever had distilled water to drink, then you have probably discovered that it doesn't taste very good. The distillation process removes the salts and dissolved gases from the water. The lack of dissolved gas makes distilled water taste flat, like a soda that has lost its fizz. The salts flavor natural waters. Although pure water might sound better than water with additives, it usually doesn't taste better. The difference between "natural" and "contaminated" as descriptions of drinking water is a fine line, one we will consider in some detail later in this course.

Let's take the chemist's perspective and consider the behavior of pure water. Water is a molecular compound. Two hydrogen atoms are connected to one central oxygen atom to make each molecule of water. The connections are called chemical bonds. The mass of a water molecule is equal to the mass of two hydrogen atoms plus one oxygen atom. The phase transition we have already considered is associated only with changes in the three-dimensional arrangement of lots of water molecules relative to one another. Chemical bonds are not affected by phase transitions, so the characteristics that describe the different phases of water are called physical properties.

One physical property that can describe any phase of water is density, the ratio of the mass of a sample divided by its volume. In the metric system, liquid water has a nominal density of 1 gram/mL. What do you know about ice, as compared to water? That's right, ice floats. Ice has a lower density than water. The density of pure, solid water at 0°C is 0.92 g/mL. If you start at room temperature (25°C) with 1 L, 1,000 mL of liquid water, and you cool it off to zero C, what happens to its volume as it freezes? In order to answer this you need to remember one thing: all the H<sub>2</sub>O molecules you started with are still in the sample, whether they are present as a solid or a liquid. The mass of the sample does not change when the phase transition occurs. If the mass stays the same, but the density goes down when the solid freezes, what must happen to the volume of the 1 L of liquid water when it freezes to ice? That's right, the volume increases. In fact, using the density information here, the volume of the frozen water will be as shown.

$$0.92 \text{ g/mL} = 1,000 \text{ g} / V(\text{ice}) \rightarrow V(\text{ice}) = 1,000 \text{ g} / 0.92 \text{ g/mL} = 1,087 \text{ mL}$$

This expansion of water when it freezes is responsible for the erosion of mountains on geologic time scales, for the formation of potholes on our highways over the course of a year, and for the splitting of water pipes in our walls over a particularly cold evening. This expansion demonstrates the spectacular strength of chemical bonds and the forces that control their three-dimensional arrangement in space. The expansion of water upon freezing is so familiar to us that we might consider it a common chemical behavior. So think for a moment about another pure chemical that you can heat so that it changes from a solid to a liquid, or cool so it changes from a liquid to a solid.

If you heat white sugar, you can convert it to a liquid. If you heat rocks a lot, like in a volcano, you can turn them into magma. You may have heard about plans to liquefy coal to produce automobile fuel. However, if you think more carefully about these processes, they are different than the melting of water. How? Well, the melting of water is reversible. You can take some ice cubes out of your freezer and put them in a glass. If they melt, you can pour the water back into the ice cube tray, refreeze the water, and get back ice cubes that look exactly like the ones you started with. However, if you cool the sugar after you melt it, you do not get white sugar back. If you cool the magma, you do not get the same rocks back. The heating of these compounds produced chemical changes, not just physical changes, in the materials. And liquefied coal is a misnomer—you need to mix other chemicals with the coal to make it liquid. In fact, you can think for a long time, but you



will probably not come up with many compounds you have encountered in everyday life that undergo reversible phase transitions. Paraffin—candle wax—is one of the few, aside from water. If you have ever melted paraffin, you should note one difference between it and water. Solid paraffin has a higher density than its liquid. When you melt it, the solid stays on the bottom of the container. Water may be the most familiar chemical we deal with on a daily basis, but when it comes to melting or freezing, it is far from the most typical. In fact, water is unique among the known chemical compounds in that its solid is less dense than its liquid. If you use water as the basis for predicating “typical” chemical behavior, you will be mistaken. Water is common, but it is far from typical.

What about converting our liquid water to a gas? Most of us have never encountered pure gas phase water. When we heat a pot of water on our stove, the gas phase water we produce is mixed with the air. Note a few things. First, the water in our pot converts slowly to a gas even if we don’t turn the heat on. You can observe this phenomenon by placing some water in a container, marking the level, and leaving it undisturbed for a few days. Unless you are in an un-air-conditioned house in the summer, the water level will decline noticeably over time. As long as the relative humidity of the atmosphere near our pot is less than 100 percent, water evaporates continuously from the pot, converting the liquid water into gas phase water. If we put a lid on the pot, the relative humidity of the air inside the pot rapidly becomes 100 percent. Under these conditions, we can stop the apparent evaporation of the water.

What behavior distinguishes the boiling point of water? Not the evaporation of water from liquid to gas; we know that is happening most of the time. We identify the boiling point when we see bubbles forming. What are bubbles? Bubbles are droplets of gas phase water inside the liquid. What does the behavior of bubbles tell you about their density? Since the bubbles rise to the surface of the liquid, it seems safe to conclude that the density of the gas is less than that of the liquid. But, unlike solid and liquid water, which have specific densities at specific temperatures, gases take the volume and shape of their containers. Therefore, the density of a gas, even at a fixed temperature, depends on the size of its container. Also, gases are compressible. You can change the volume that a fixed number of gas molecules occupy or pack more gas molecules into a fixed volume by pushing on them. Because the density of gases vary, chemists specify standard conditions, called “standard temperature and pressure” (STP), so they have a basis on which to compare different gas samples. Standard temperature and pressure are defined as 0°C and 1 atmosphere of pressure. One atmosphere is the typical air pressure at sea level around the world. It is equivalent to a barometric pressure of 29.9 inches or 760 mm of mercury. The density of pure water vapor at STP is  $8.0 \times 10^{-4}$  g/mL. Because gases expand as they get hot, the density of gas phase water at 100°C and 1 atmosphere is less than this,  $6 \times 10^{-4}$  g/mL. The properties of steam are critical to modern industry. They were so fundamental in the industrial revolution that they are extensively tabulated in steam tables, available from a variety of sources.

What other common liquids evaporate into gases? The ones that usually come to my mind are gasoline and alcohols. These chemical compounds (gasoline is actually a mixture of a number of different compounds) evaporate from open containers. Interestingly, motor oil and cooking oil are much less likely to evaporate. However, have you ever boiled gasoline or alcohol? Probably not. Why not? Because heating chemical compounds can do more than cause phase transitions; it can facilitate the chemical transformation we call combustion. Hot gasoline, like hot alcohol, can burn or explode in the presence of air. Don't try to measure the normal boiling points of gasoline or alcohols at home.

Thus far we have considered the observable, macroscopic behavior of water and some other chemical compounds. But the point of science is not to simply collect observations, but to build models that allow us to explain the behavior we have observed and predict behavior we have not. Systematic application of the scientific method has resulted in an enormous improvement in our understanding of chemical behavior over the past two hundred years or so. In this course, we will use modern chemical models to explain the unique behavior of water and expand our study from this most familiar of chemicals to those that exhibit more typical, but also more exotic, properties. We will highlight a variety of the advances of the past two hundred years. We'll consider both the conceptual and the mathematical aspects of the models. We will review our current understanding of chemistry within the framework of a typical college or university introductory course, and we will discuss the twenty-first-century applications pushing modern chemistry almost to the realm of magic abandoned by eighteenth-century alchemists.

How do the modern models of chemistry account for the behavior of water? Let's start with some fundamentals. Water contains two hydrogen atoms and one oxygen atom chemically bonded together. What are atoms? Atoms are the smallest pieces of the chemical elements. Everything you can see, touch, taste, or smell is made of some combination of the atoms of the one hundred fourteen (two new elements were announced in June 2011) known elements.

Until Dalton proposed his atomic theory in 1808, the prevailing model, consistent with most observations, was that matter was continuous. The water on your stove is noticeable because of the space it fills; the pot that contains it appears absolutely solid. However, modern chemistry views matter as composed of discrete atoms. And modern physics tells us that atoms are mostly empty space.

If atoms are mostly space, how do they manage to assemble into things that appear to be solid? Modern science tells us that atoms and molecules are fundamentally electrical in nature. You can demonstrate the electrical nature of large collections of atoms to yourself in a number of ways. Brush your hair enthusiastically on a dry day, and it may stand off from your head. Cut a plastic bag into 1 cm wide strips, hang one strip evenly over your finger, and place two fingers from your other hand loosely around one side of the plastic. Quickly slide your fingers down one side of the plastic, without pulling the plastic off your finger. Continue past the end of the plastic so the ends are free. What happens? Or rub a

balloon on your sleeve and then hold it over some small bits of paper on a table, or place it against a wall.

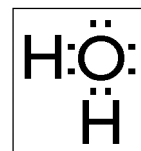
All of these physical activities produce charge separations in the molecules that make up the materials. Like charges repel each other; opposite charges attract each other. When you brush your hair, the hairbrush acquires one charge and your hair another. When many hairs have the same charge, they repel each other. The balloon gains negative charges from the cloth it is rubbed on. These negative charges induce a charge separation in the bits of paper, or on the surface of the wall, and the attraction between the opposite charges is sufficient to attract the paper to the balloon or the balloon to the wall.

Today the atomic theory is accepted as a correct picture of the chemical elements. The atomic theory states that atoms are composed of subatomic particles, which were first isolated between 1879 and 1932—the positively charged proton, the negatively charged electron, and the electrically neutral neutron. The charge on the electron and proton are equal in magnitude, but opposite in sign. We call the magnitude a *unit charge*. The electron is negatively charged and the proton is positively charged. The mass of the proton and neutron are almost identical, but the electron is the lightweight member of the group, weighing 1/1,800th as much as the other subatomic particles. The structure of the atom was not determined until the quantum revolution, which began at the end of the nineteenth century, but it made the first half of the twentieth century the age of the nucleus. Today, we know that all atoms have a central nucleus that contains all its positive charges and the vast majority of its mass. The nucleus is surrounded by electrons that occupy a space which is huge compared to the size of the nucleus. All atoms of a given element have the same number of protons in the nucleus. The number of protons is called the atomic number, the integer at the top of the block on the periodic table. Hydrogen is atomic number 1 because each hydrogen atom contains one proton in its nucleus. Gold, Au, is atomic number 79, because each gold nucleus contains 79 protons. To be electrically neutral, an atom must have the exact same number of electrons as protons. However, two atoms of the same element can have different masses if they have different numbers of neutrons in their nuclei. Hydrogen is the lightest of the elements. It contains one proton and one electron when it is electrically neutral. Oxygen atoms contain eight protons and eight electrons when they are electrically neutral. If you took a chemistry class in school, you will remember the periodic table. The periodic table organizes all the known elements in order according to the number of protons in their nuclei. The rows of the periodic table are called periods; the columns are called groups. A periodic table provides a rich source of information about atoms, their physical properties, and their ability to form chemical compounds.

The electron-shell model describes how the electrons are organized around their nuclei. The atomic nucleus occupies only a minute fraction of the total volume of the atom. The greatest part of the atom is occupied by the electrons. If you consider the nucleus to be a pea, a typical atom would be about the size of a Major League Baseball stadium. Because the electrons are on the outside of the atom, they are responsible for most of chemistry.

The electrons can be separated into two categories. The *core* electrons are physically near the nucleus and so strongly attracted to it that they essentially never participate in chemical processes. The outer, or *valence*, electrons are on average farther from the nucleus and shielded from its total positive charge by the core electrons. It is these outer or valence electrons that are rearranged in chemical processes. The periodic table reflects the valence electron structure of atoms. As you move from left to right across a period, the number of valence electrons goes up. The elements in the left-hand column, called the alkali metals, each have one valence electron. All the elements in each group on the periodic table have the same number of valence electrons (except for element 2, Helium, which has only two, while the other noble gases have eight). For example, all the elements in column 16 or group VI: O, S, Se, and so on, have six valence electrons. Most chemists think of atoms as small squishy spheres with their size given by an average radius. As you go down a group on the periodic table the radius of the atoms increases, as you would expect. But as you move horizontally across a period, the radius of the atoms varies with increasing atomic number in a more complicated way and in general decreases. We'll consider the factors that affect the size of the atoms in more detail in lecture 5.

In 1916, Gilbert N. Lewis proposed an electron dot model for showing the distribution of the valence electrons in molecules. Today the electron dot model is ubiquitous in chemistry and allows us to both explain and predict the structure of covalent compounds. In addition, it provides the underlying motivation for the “structure = function” hypothesis that continues to revolutionize modern molecular biology. To use Lewis's model, you need to know the chemical symbols of the elements and the number of valence electrons each element has. The majority of the molecules we will discuss in this series of lectures will be composed of the elements hydrogen, carbon, nitrogen, oxygen, fluorine, phosphorous, sulfur, and chlorine. These atoms form molecules when their valence electron shells physically overlap in space. The overlay allows the atoms to share a pair of bonding electrons between their nuclei. At its most simplistic, locating a pair of electrons between two nuclei provides an electronic attraction; the negative electrons provide a glue to hold the positive nuclei together.



Lewis Dot Model

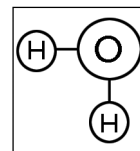
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Lewis's dot diagrams show that the atoms in molecules prefer to have eight valence electrons, an octet of valence electrons. Lewis's diagrams arrange these eight electrons in four pairs, except when the element is hydrogen, which only attracts one pair of electrons. In water, the central oxygen atom contributes six valence electrons and each hydrogen atom contributes one valence electron for a total of eight electrons in each molecule. The Lewis dot diagram for water shows the O in the middle, and on each of the four sides of an imaginary square drawn around the oxygen a pair of electrons is shown as two dots. Two of the pairs of electrons have H's drawn next to them, showing the positions of the hydrogen atoms. The electrons shared between the oxygen and a hydrogen are called “bonding electron pairs.” The electron pairs that are not shared are called “nonbonding” or “lone” pairs. The Lewis diagram is a two-dimensional representation of a three-

dimensional molecule. The electron pairs determine the three-dimensional geometry of molecules. Four pairs of electrons can stay the farthest apart in space by pointing toward the corners of a tetrahedron. You might remember that the tetrahedron is the simplest of the Platonic solids; its surface is composed of four identical equilateral triangles joined at the edges to form a solid with four triangular faces and four vertices. The oxygen in water sits in the center of the tetrahedron, while the electron pairs, bonding and nonbonding, point toward the four corners. Two of the corners are occupied by the H atoms sharing the electron pairs. In water, the distance between the center of the oxygen atom and the center of a hydrogen atom is 94 pm. We say the bond length is 94 pm. The bond angle defined by the lines connecting the oxygen to the two hydrogens is  $104.5^\circ$ , not far from the tetrahedral angle of  $109.5^\circ$ . We consider the water molecule to have a bent or V-shaped geometry, because the molecular geometry describes the relative positions of the nuclei in the molecule. However, the tetrahedral distribution of the four electron pairs around the oxygen is the dominant reason that water exhibits its unique properties.

Similar simple models illustrate the structure of methane,  $\text{CH}_4$ ; ammonia,  $\text{NH}_3$ ; hydrogen fluoride, HF; and hydrogen chloride, HCl. In methane, the carbon has four valence electrons, and the four hydrogens provide the other four electrons to complete the octet of electrons around the central carbon atom. The molecule has a tetrahedral structure, with a hydrogen at each corner and the carbon in the center. In ammonia, the central N atom provides five valence electrons; therefore, only three more are needed to give the nitrogen an octet. To draw the Lewis diagram of ammonia, draw five electron dots around the N. Then complete the octet by drawing three H atoms and their valence electron dots to complete the octet. The four electron pairs around the N point to the corners of a tetrahedron. The ammonia molecule's geometry is called a triangular pyramid. Think of turning the molecule until its three hydrogens are on a tabletop. The three hydrogens form a triangle. The nitrogen in the center of the tetrahedron is above the plane defined by the three hydrogens, so the molecule has a pyramidal structure. The lone pair of electrons on the nitrogen points vertically upward. Fluorine is a halogen, in column seven on the periodic table. It has seven valence electrons, and combines with only one H atom to get an octet. The HF molecule is considered to have a linear geometry, even though the four electron pairs around the fluorine point toward the corners of the tetrahedron.

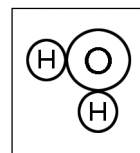
Sometimes the Lewis diagrams are simplified to ball and stick representations. In the ball and stick version, the balls represent atoms and the sticks the electron pairs they share. As a substitute for more expensive, sophisticated kits, you could use marshmallows, gum drops, or Styrofoam balls to represent atoms and toothpicks to represent electron pairs to build molecular models. Ball and stick models are convenient for illustrating geometric features of molecules, but atoms really occupy space, so the bonding of atoms in molecules is more accurately represented by space-filling models, where the atoms appear smashed together like compressible balls. In using either of these model techniques, the relative position of the nuclei of the atoms defines the molecular geometry.



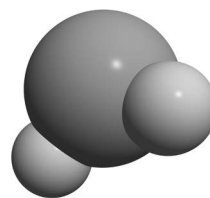
Ball and Stick Model

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More sophisticated, computer-generated models of molecules are available to chemists today. The computer models can replicate the Lewis dot pictures, the ball and stick pictures, or the squished ball pictures. But they can also provide much more information, showing how the electron distribution varies throughout the space around the atomic nuclei that the molecule is composed of, or how an imaginary positive test charge approaching the molecule responds to the electrical environment of the molecule. A popular molecular illustration uses a rainbow of colors from red-orange-yellow-green-blue to violet to illustrate the force experienced by a test charge as it moves around in space near a molecule. The picture of a water molecule in this model shows the variation in the electrical environment. The test charge is strongly attracted to the side of the molecule occupied by the lone pairs of electrons, but much less attracted, or even repelled, by the side of the molecule where the hydrogens are located. A single water molecule therefore ranges in color from red at the side where the lone pairs of electrons are to violet-blue at the tip of the region occupied by the hydrogen atoms. The space-filling model of the ammonia molecule is similar to that of the water molecule, but the violet-blue region is larger, corresponding to the larger number of hydrogens bonded to the nitrogen. In contrast, the methane molecule is pretty uniformly blue all around, with some green regions between the pairs of hydrogen atoms. Molecules that show a systematic change across the colors of the rainbow are said to be polar molecules. A polar molecule is one in which the center of the positive charges from the nuclei and the center of the negative charges from the valence electrons is not in the same place. Water and ammonia are both considered to be polar molecules. Methane is considered to be nonpolar, as are all hydrocarbons—molecules made only of atoms of hydrogen and carbon covalently bonded together.

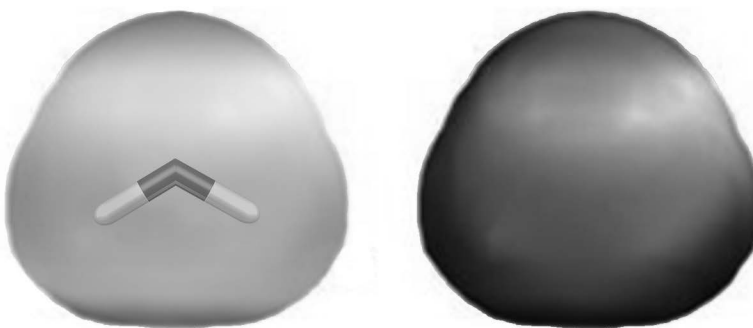


Space-Filling Model



Space-Filling 3D Model

Chemists generally describe the polarity of molecules as arising from the polarity of individual chemical bonds. Atoms do not necessarily share the valence electron pair that forms the bond between them equally. Some atoms really, really want their partner's electron. Some are very willing to give their electron away. The extent to which atoms attract shared electron pairs to themselves was first discussed quantitatively by Linus Pauling. Pauling defined the electronegativity of an atom as a measure of its tendency to attract electrons to itself. Pauling assigned the highest electronegativity, 4.0, to the electron pig of the periodic



Electrostatic Model

table—fluorine. Electronegativity decreases down each group of the periodic table, and as you move from right to left across each period. You can think of the covalent bond as a tug of war between the two nuclei for the attention of the electron pair that makes the bond. In water, hydrogen has a medium electronegativity of 2.2, but oxygen, fluorine's neighbor, has a high electronegativity, 3.4. Therefore, when hydrogen and oxygen share an electron pair, the electrons spend more of their time near the oxygen, and we say that the OH bond is a polar bond. Interestingly, although oxygen is quite electronegative, when two oxygen atoms bond together, they share their electrons equally. We say the oxygen molecule is nonpolar. Continuing our quest to be quantitative in this discussion, we can assign a dipole moment to a polar bond. The dipole moment is a measure of the magnitude of the charge separation in the bond multiplied by the distance separating the positive and negative centers. The dipole moment is generally represented superimposed over a molecular model by drawing an arrow that points from the less electronegative atom to the more electronegative. It has both a magnitude and a direction, and it is therefore considered a vector quantity by scientists. In contrast, mass and volume are considered scalar quantities. They are described by a numerical value, a magnitude only.

In order to have a polar molecule, you must have some polar bonds. But the converse is not true. If we replace the hydrogens in our methane molecule with four fluorine atoms, we see that the tetrafluoromethane molecule has four polar bonds, with the bond moments pointing from the carbon toward the more electronegative fluorines. But because the fluorines are located at the corners of a tetrahedron, the four vectors exactly cancel each other out, and the tetrafluoromethane molecule is nonpolar. If you have trouble imagining this in three dimensions, consider the two-dimensional projection. If we had four exactly equivalent teams pulling to the north, south, east, and west on a single tug-of-war rope with four handles, the center of the rope would not move. The balance in the “pulls” in the tug of war is an exact analogy for the balance of forces the electrons in tetrafluoromethane experience, and the result is that the molecule is nonpolar.

Before we turn our attention to a chemical consideration of the scale of water molecules and their energetics, let's look at some fun facts. You probably have heard that all snowflakes are six sided, and no two snowflakes are alike. It turns out this is pretty much true. Kenneth G. Libbrecht, a physicist at the California Institute of Technology (CalTech), used a specially designed snowflake photomicroscope to take thousands of pictures of both naturally falling and laboratory-made snowflakes. His study pretty much confirmed the adage that no two snowflakes are alike. Given that all water molecules are identically the same shape and size, this may give you some indication of how many water molecules make up a single snowflake.

Those of you who are science fiction fans are probably wondering how Kurt Vonnegut's creation of ice-nine in his novel *Cat's Cradle* compares with reality. There actually is an ice-IX. However, thankfully, it lacks the stability that Vonnegut ascribes to it in *Cat's Cradle*. Actually, there are seventeen known solid forms of ice. The fact that we really only

encounter one of them with any regularity illustrates how little of the physical universe we experience directly. The known forms of ice exist over temperatures and pressures that span an enormous range from near absolute zero on the temperature scale and a fraction of a millibar of pressure to 400°C (673°K) and 10 Mbar (mega bar,  $10^6$  bar) of pressure. These conditions include those at which we expect to find molecular water in locations ranging from the vastness of outer space to the bottom of glaciers.



## For Greater Understanding

### Questions

1. Which is the chemical formula of water?  
a. HO      b. H<sub>2</sub>O      c. HO<sub>2</sub>
2. When 1,000 g of ice melts to form water at 0°C, what volume does it occupy?
3. According to the periodic table, the average atom of hydrogen has a mass of 1.008 amu (atomic mass units). The average atom of oxygen has a mass of 16.00 amu. What is the mass of a single water molecule in amu? The conversion factor for converting between amu and grams is  $1 \text{ amu} = 1.6605 \times 10^{-24} \text{ g}$ . How many grams does one water molecule weigh?
4. Draw a picture of tetrachloromethane, CCl<sub>4</sub>. The carbon is connected to each of the chlorines. Are the carbon-chlorine bonds polar? Is the molecule polar? Explain your reasoning.

### Suggested Reading

American Chemical Society, and Jerry A. Bell. *Chemistry: A General Chemistry Project of the American Chemical Society*. New York: W.H. Freeman, 2005.

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### Other Books of Interest

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Libbrecht, Kenneth George. *Ken Libbrecht's Field Guide to Snowflakes*. Minneapolis, MN: Voyageur Press, 2006.

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## Lecture 2

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### Aqueous Solutions

The Suggested Readings for this lecture are the American Chemical Society and Jerry A. Bell's *Chemistry: A General Chemistry Project of the American Chemical Society*, chapter 2: "Aqueous Solutions and Solubility," and Linus Pauling's *General Chemistry*.

#### Solutions

Life is possible because of the chemical compounds that are soluble in water, and because of those that are not. In lecture 1, we considered the structure and properties of pure water. In this lesson, we will consider aqueous solutions. Aqueous solutions are composed primarily of water, but they also contain other chemicals dissolved in the water. We will examine the characteristic behaviors of solutions, the chemical forces responsible for those characteristics, the energy considerations that drive their formation, and the terminology that chemists use to describe solutions.

Take a few moments and make a list of some substances that you know are soluble in water. List some that are not.

You probably identified salt and sugar among the substances that dissolve in water. Perhaps you included oil—cooking or motor—and flour among substances that do not. Let's formalize the definitions of the terms we are using here. A solution is a homogeneous mixture of a solvent, the substance present in excess, and one or more solutes, the substances uniformly distributed throughout the solution because they dissolved. Homogeneous or homogenous means the solution is uniform in its composition and properties throughout the solution. Homogeneity is a macroscopic property of solutions; you can discern it by looking at the sample. In solutions, the macroscopic observation is explained by the microscopic structure. On a microscopic level, each of the solute components in a homogeneous solution is completely surrounded by water molecules. Other solutions are described as heterogeneous. They look like they are composed of a variety of components; say a sample of sand and water scooped up in a pail at the beach. Our primary interest here is in homogeneous solutions.

Why are salt and sugar soluble in water while oil and flour are not? You have probably heard the adage "like dissolves like." But what exactly is "like" between water and sugar? What is unlike between oil and water? To answer these questions, we need to consider the structure of the sugar and oil molecules. There are three important intermolecular forces—hydrogen bonding, polar attractions, and London dispersion forces. The extent to which solutes and solvents are "alike" depends on the structure of their molecules. The more similar the intermolecular forces between the solvent and the solute molecules, the more soluble the solute is in the solvent. Hydrogen bonds can only form when molecules have hydrogen directly bonded to O, N, or F. Polar attractions are important in asymmetrical

molecules with polar bonds and dipole moments. All molecules have dispersion forces, and dispersion forces increase with the number of electrons in the molecule. Because the structure of molecules is important in determining the intermolecular forces they experience, chemists often examine the Lewis dot diagrams of molecules to describe the forces. Alcohols are an important category of molecules that have solubility properties clearly related to their structures. An alcohol is a compound containing one or more carbons and at least one oxygen bound to hydrogen. Some commonly available alcohols include methanol,  $\text{CH}_3\text{-OH}$ , an ingredient in gasoline additives; ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , the alcohol in alcoholic beverages; and isopropyl alcohol,  $\text{C}_3\text{H}_7\text{OH}$ , the alcohol in rubbing alcohol. But chemists know of many other alcohols, including pentanol,  $\text{C}_5\text{H}_{11}\text{OH}$ ; hexanol,  $\text{C}_6\text{H}_{13}\text{OH}$ ; and octanol,  $\text{C}_8\text{H}_{17}\text{OH}$ . In my classroom, students take test tubes, distilled water, and dropper bottles full of a variety of alcohols and test the solubility of each. If twenty drops of alcohol dissolve in 1 mL of water, the alcohol is highly soluble. If only five drops dissolve, and the sixth drop forms a separate phase, the alcohol is slightly soluble. If the first drop of alcohol forms a visible separate layer, then the alcohol is insoluble in water.

In keeping with the structure-function approach we considered in lecture 1, let's consider the solubility of a series of compounds called "normal" alcohols. Normal alcohols have their carbon atoms all hooked together in a straight chain. Each carbon is attached to two hydrogen atoms, and two carbon atoms, except the ones on the end. One end carbon shares its fourth valence electron with a hydrogen. The other shares its fourth valence electron with an oxygen atom, which in turn shares its sixth valence electron with another hydrogen atom. The  $\text{-OH}$  bond at the end is characteristic of normal alcohols. Chemists name these compounds according to the number of carbons they contain. In order, the first eight normal alcohols are methanol, one carbon; ethanol, two carbons; propanol, butanol, pentanol, hexanol, heptanol, and octanol, eight carbons. In your mind's eye, draw a Lewis dot picture of methanol. On one side of the carbon is a  $\text{-OH}$  group, which looks like half a water. On the other side is a  $\text{-CH}_3$  group, which is nonpolar and does not look like water at all. In the classroom, if you started adding drops of methanol to 1 mL of water, you could add as many as you like, until you ran out of methanol, and the two compounds would form a solution. You would never see a separation between the water and the alcohol phases. In fact, if you started with pure methanol and added water, you would observe the same thing. Methanol and water are miscible—they form a solution in any proportion. Despite the fact that only one half of the methanol molecule looks like water, the two molecules are enough alike that you don't see a phase separation between them.

Let's move on to ethanol, the alcohol in alcoholic beverages. Ethanol contains two carbons and one  $\text{-OH}$  group. The  $\text{-OH}$  group still looks like half a water molecule, but in comparison to methanol, the hydrocarbon component in ethanol is twice as big. Ethanol looks less like water than methanol. But it still looks enough like water to be highly soluble in the classroom test. Again, you can mix any amount of water with any amount of ethanol, and you will have a solution form. As you increase the number of carbons in the alcohols,

the part that looks like half a water molecule becomes less important in determining the overall behavior of the molecule. In the classroom, students start to observe the presence of two layers when they add a few drops of butanol to the water. By the time they move up the ladder to octanol, most students will observe a separate layer when the first drop of octanol is added to 1 mL of water. By this crude test, octanol appears insoluble in water. The hydrocarbon chain in octanol overwhelms the  $\text{-OH}$  group, and the molecule is not enough like water to be soluble.

Table sugar, sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , has a complicated ring structure. In sucrose, five carbons and an oxygen atom form a ring that bridges through an oxygen atom to connect to a second ring made of four carbons and an oxygen. The carbons need extra partners to fill their valences, and there are eight  $\text{-OH}$  groups in the molecule. The eight OH's make sugar look enough like water that sucrose is actually more soluble in water than its simpler cousin, glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , which contains only one six-member ring. The eight  $\text{-OH}$ 's provide eight sites per molecule for hydrogen bonding to occur. Sucrose is very soluble in water.

Let's return to our ethanol example for a moment. The chemical formula for ethanol is  $\text{CH}_3\text{CH}_2\text{OH}$ . Remember that the  $\text{-OH}$  group on the end is the structural feature that makes a compound an alcohol. If we take the atoms of the ethanol molecule and rearrange them, we can come up with an alternate structure that satisfies all of Lewis's rules— $\text{CH}_3\text{-O-CH}_3$ . Note that both ethanol and this new compound contain two carbons, six hydrogens and an oxygen atom. In both, all the atoms have satisfied their octets. We can put the oxygen between the two carbons and hook the six hydrogens up to the two carbons to fill their valence requirements. Compounds that contain the same number of specific atoms, but have those atoms bonded differently so they are arranged differently in three-dimensional space, are called "structural isomers." Note that  $\text{CH}_3\text{-O-CH}_3$  does not have a hydrogen atom bonded directly to an oxygen atom. The compound is called dimethyl ether. It is not an alcohol and it does not enter into hydrogen bonding. Its geometry is similar to water's geometry. Because of the tetrahedral arrangement of electron pairs around the central oxygen atom, the molecule is bent. The angle formed when you draw lines from the oxygen nucleus to the carbon nuclei is close to the tetrahedral angle of 109.4 degrees.

Dimethyl ether is a polar molecule, but it does not have hydrogen bonds. It is a gas at room temperature and pressure, and it is slightly soluble in water ( $71 \text{ g dm}^{-3}$  at  $20^\circ\text{C}$ ), but it is not as soluble as ethanol. If we replace the O in the middle of dimethyl ether with a  $\text{CH}_2$  group, we have  $\text{CH}_3\text{-CH}_2\text{-CH}_3$ , propane. Note that propane has the same number of electrons as dimethyl ether. The angle between the end carbons and the central carbon is still 109.4 degrees. But propane is a hydrocarbon, it is nonpolar, and it has only weak van der Waals forces between its molecules. It is a gas at room temperature and pressure. Propane is essentially not soluble in water. (Solubility is 0.007 g propane per 100 ml of water at 1.013 bar and  $20^\circ\text{C}$  [ $68^\circ\text{F}$ ].)

Motor oil is not soluble in water, either. Motor oil is a mixture of a number of different hydrocarbons, all longer than propane. A typical molecule in motor oil might have sixteen

carbons and thirty-four hydrogens all strung together, the carbons acting like the beads of a necklace, and the hydrogens filling their octets like little extra decorations on each bead. The entire molecule acts like a wet spaghetti noodle—it sticks to others like itself, tends to coil up on itself in an aqueous environment, and eschews water whenever possible. In contrast to ethanol, which is described as hydrophilic (water loving),  $C_{16}H_{34}$  and its hydrocarbon brethren are described as hydrophobic (water fearing).

Although we have described the van der Waals or dispersion forces as relatively weak, these intermolecular forces are strong enough to determine the physical properties of hydrocarbons. The viscosity and boiling point of hydrocarbons increase with the number of carbons in the chain, the mass of the molecule, or the number of electrons in the molecule, however you want to count.

Vegetable oils are chemically both quite similar and quite different from petroleum oils. The fat component in vegetable oil is a triglyceride, not a hydrocarbon. You can think of a triglyceride as a glycerol molecule with acids attached to it. Structurally, a glycerol is a tri-ol, a propane, except that each carbon atom has a  $-OH$  replacing one hydrogen. We can write its formula as  $CH_2(OH)CH(OH)CH_2(OH)$ . If you draw the Lewis dot diagram for this structure, you will see there is only one structural isomer. The picture might look different on paper, but when you think of it in three dimensions, the molecule is completely flexible and can easily wiggle around so all its  $-OH$  groups are on the same side of the molecule, or each is headed off in a different direction. The  $-OH$  functional group is the same one that makes alcohols alcohols. When it functions as the basis of a triglyceride, the  $-OH$  groups on the glycerol are replaced by fatty acids. A fatty acid is cousin to a long-chain alcohol. It has a long hydrocarbon chain. Typical oils produced in animals and plants have sixteen, eighteen, or twenty carbons and enough hydrogens to fill all but one of the carbon's valences. At one end, however, is a carboxylic acid group. The last carbon is bonded to two oxygens, one shown on the Lewis diagram as a double bond, the other as a single bonded oxygen, which has its valence filled with a hydrogen when the fatty acid molecule is independent. However, when constructing the oil molecule, the glycerol and the fatty acid come together—the  $-OH$  on the glycerol and the carboxylic acid on the fatty acid—so that structurally the valence on the single-bonded oxygen from the fatty acid is now filled by a direct connection to the carbon on the glycerol. The reaction spits out a water molecule and is therefore classified as a dehydration. When three fatty acids connect to one glycerol, the molecule is called a triglyceride. In oils, the three fatty acids are often different. Their most important feature, both physiologically and from a physical properties standpoint, is whether the fatty acids are saturated or unsaturated. Saturated fatty acids, like saturated hydrocarbons, contain only single C-to-C bonds. Unsaturated fatty acids or unsaturated hydrocarbons contain one or more pairs of carbons connected by double or triple bonds. Instead of being “saturated” with hydrogen, some of the carbon valence is satisfied by multiple bonds between adjacent carbon atoms. The multiple bonds have a substantial impact on both the geometrical shape of the molecules and their physical properties. Multiple bonds do not allow free rotation. They restrict the geometry

of the molecule and prevent it from curling up like a wet noodle. The more unsaturated a fatty acid, the more rigid it is and the more likely it is to form a solid when pure and the less soluble it is in water.

So we see that the adage “like dissolves like” means that covalent molecules that have enough hydrogen bonds or are polar enough are more soluble in water than nonpolar compounds. However, in lecture 1 we saw that there is another class of compounds, held together not by sharing electrons but by trading them to form ions. How does the solubility of ionic compounds in water compare to that of covalent compounds?

Chemically pure water contains so few charged particles that it is an electrical insulator. It does not conduct an electrical current, nor does a solution of sugar in water, nor a solution of alcohol in water. But a solution made by dissolving salt in water is different. A crystal of sodium chloride, salt, is a three-dimensional crystal of alternating positive sodium cations and negative chloride anions. When the salt dissolves in water, the sodium cations and the chloride anions separate into a dispersed set of charged particles. Because water is highly polar, the water molecules are attracted to the ions from the salt. In general, the positive ends of water molecules near the negative ions orient themselves toward the anions. The negative ends of water molecules are attracted to the cations. Although the arrangement is far from rigid, the preference is clear. The water molecules are said to form hydration layers around both types of ions. The hydration layer helps to keep the oppositely charged ions separated from each other in the solution. When you dissolve even a small amount of salt in water, the resulting solution conducts electricity much more efficiently than pure water or a solution of sugar in water, or a solution of alcohol in water. A system that conducts electricity contains charged particles that are free to move under the influence of an electrical field and is called an electrolyte. A solution that does not contain charged particles is called a nonelectrolyte. You are probably familiar with the term *electrolyte* from advertising for sports drinks. The human body contains lots of electrolytes. When athletes exert themselves, they sweat out both water and the salts present in their system. Sports drinks replace both.

So are all ionic solids soluble in water? No. Let's consider some basic information about ionic compounds, and then it will be easier for us to discuss the characteristics that make some ionic compounds soluble and some insoluble in water. Binary ionic compounds form when elements from opposite sides of the periodic table have had the opportunity to complete their octets by donating or accepting electrons from a partner so that both species end up with an octet of electrons in their outer shells. The elements on the left side of the periodic table, the metals, have a few too many electrons and prefer to give those electrons away, forming positively charged cations. The number of electrons given away is equal to the number of the column the metal atom occupies on the periodic table. Sodium forms a +1 cation, calcium a +2 ion, and aluminum a +3 cation. The nonmetals on the right side of the periodic table are happy to accept extra electrons and form negatively charged anions. Their charge is determined by the number of columns they are away from group

VIII or XVIII. Fluorine forms a  $-1$  ion, oxygen a  $-2$  ion, and nitrogen a  $-3$  ion. When ionic compounds are formed, the net charge on the compound has to be zero. When binary ionic compounds are named, the cation comes first and the anion second. The cation has the same name as its metal; the anion changes endings to “ide.” So the compound of sodium and chlorine is sodium chloride, NaCl. The compound of calcium and chlorine is calcium chloride. Chemists know that the charge on calcium is  $+2$  and that the formula for calcium chloride is  $\text{CaCl}_2$ , but there is nothing in the name that tells you that the ion ratio is not the same as in sodium chloride. Aluminum chloride is  $\text{AlCl}_3$ . Since ionic solids do not form molecules, the numbers here just give the ratio of the number of cations to the number of anions that must be present to make a neutral salt sample. Because the net charge in a large collection of formula units is zero, crystals of ionic compounds are electrically neutral.

In general chemistry courses, there are a number of polyatomic ions that are important in ionic solids. Important polyatomic cations include the ammonium cation,  $\text{NH}_4^{+1}$ . Important polyatomic anions include carbonate,  $\text{CO}_3^{-2}$ ; hydroxide,  $\text{OH}^{-1}$ ; nitrate,  $\text{NO}_3^{-1}$ ; phosphate,  $\text{PO}_4^{-3}$ ; and sulfate,  $\text{SO}_4^{-2}$ . The ammonium cation consists of one N atom and four hydrogen atoms covalently bonded together. If you try to draw the Lewis diagram for ammonium ion, you will note that nitrogen brings five valence electrons to the picture, and each hydrogen one. So  $\text{NH}_4$  has nine, not eight, valence electrons. If it can give one away to another species, the covalently bound unit can get a stable octet. That is why the species  $\text{NH}_4$  is stable when it has a  $+1$  charge. In contrast, an oxygen combined with a hydrogen is short an electron. If the system can find an extra electron, it can form a stable species that satisfies the octet rule, so the formula for the hydroxide ion is  $\text{OH}^{-1}$ . In ionic crystals or in the aqueous solutions they form by dissolving in water, the covalently bound polyatomic anions and cations hold together as specific units and are solvated by water molecules in the same way that monatomic ions are. There are vast numbers of stable polyatomic ions, but we will only consider the ones mentioned here in this course. Chemists recognize the polyatomic ions in chemical formulas. They know that  $\text{MgCO}_3$  is magnesium carbonate, where  $\text{Mg}^{+2}$  ions are attracted to the negatively charged carbonate anions. But if we write the formula for the compound ammonium sulfide, we need to realize that it takes two ammonium cations to balance the minus-two charge on the sulfide. To make it a little easier to distinguish the numbers indicating the polyatomic ion structure from the number of polyatomic ions in the formula, a parenthesis is placed around the polyatomic ion, and the number of polyatomic ions present is subscripted outside the parenthesis. The formula is written  $(\text{NH}_4)_2\text{S}$ . The formula unit contains two nitrogen atoms, and eight hydrogen atoms assemble as two  $\text{NH}_4^{+}$  units, balancing the negative-two charge on the sulfide anion. A parenthesis is placed around the polyatomic ion for clarity. The compound sodium phosphate is written  $\text{Na}_3\text{PO}_4$ . There is no parenthesis because more than one monatomic cation— $\text{Na}^{+}$ —is present, but only one phosphate ion  $\text{PO}_4^{-3}$  is present to balance the charge.

If you have access to a chemistry lab, it is pretty easy to collect a large sample of ionic compounds and run simple experiments to see which ones dissolve in water. Just as

Mendeleev looked for patterns of behavior among the elements to organize the periodic table, we can look for patterns of behavior in the solubility of ionic compounds to derive solubility rules. In general, we find that all sodium salts are soluble, as are all potassium salts and all the ionic compounds with chloride or bromide or nitrate as their anions. Things get a little bit more complicated when the ions in our compounds have multiple charges. For example, some calcium and magnesium salts are insoluble. In fact, you are very likely to be familiar with the insolubility of calcium carbonate and magnesium carbonate if you live where the natural waters are high in mineral content. We call this hard water. The calcium and magnesium in the natural waters in your region form deposits when carbonate is also present.  $\text{MgCO}_3$  and  $\text{CaCO}_3$  are the principal components in the hard-water spots that form when your water evaporates, or when you boil down the water in your teakettle, leaving only the deposit of formerly dissolved salts behind. In a gross generalization, we can say that ionic compounds containing multiply charged cations and anions are least likely to be soluble in water. Ionic compounds of singularly charged ions are most likely to be soluble. But please note one thing. In our definition of “solubility,” we are depending on our ability to observe macroscopic changes. We’ll return to a more microscopic picture of solubility later in this series.

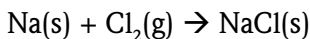
Most chemists consider the dissolution of a soluble salt in water to be a physical transformation, not a chemical transformation. It is a physical transformation because it simply involves the physical arrangement of the chemical components, not their transformation into other chemical forms. Dissolving a salt in water has some similarities with melting ice. The building blocks don’t change; they just get rearranged. But when two salt solutions are mixed together, then we can initiate a chemical transformation. Say we have a solution made by dissolving calcium chloride in water and another solution made by dissolving sodium sulfate in water. Both of these solutions look like water to our eye. But if we test their ability to conduct an electrical current, we find them highly conductive, and therefore quite different from water. When we mix them together, a magical transformation occurs! A snowstorm forms in the container holding the mixture. After a few minutes, the snow settles to the bottom of the container, forming a layer of powdery white solid on the bottom of the container. We call the solid a precipitate. The clear solution on top is called the supernatant. If we test the supernatant, it still conducts electricity. What forms the white solid? Why does the supernatant still conduct electricity? If we consult the solubility rules we discussed a few minutes ago, we can answer these questions.

The calcium chloride dissolved in solution, forming calcium  $+2$  ions and twice as many chloride  $-1$  anions. The sodium sulfate dissolved, forming twice as many sodium  $+1$  ions as sulfate  $-2$  anions. Recall that we said that all salts of sodium and all chlorides were soluble. However, when we mix the two solutions together, there are four ions in the single solution that results. It contains sodium ions, sulfate ions, calcium ions, and chloride ions. Opposites still attract. And the calcium and sulfate ions are very strongly attracted to one another. They both have a charge of 2 (calcium is  $+2$  and sulfate is  $-2$ ). Physicists describe the attraction

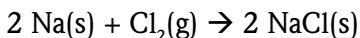


between oppositely charged particles using Coulomb's law—the force of the attraction is proportional to  $Q_1 \times Q_2/r^2$ . The attraction between calcium and sulfate is therefore four times stronger than the attraction between sodium and chloride, all else being equal. This attraction is sufficient for the calcium and sulfate ions to make their way through the sea of water molecules surrounding them, find each other, and fall together in a joyous storm of precipitate. We say that calcium sulfate is insoluble, not soluble, in water. In addition to leaving hard-water deposits in our plumbing, the insoluble ionic compound calcium carbonate,  $\text{CaCO}_3$ , forms the shells we pick up on the beach, the limestone steps at city hall, and the crystals in the balance organs of your inner ear. The insoluble salts calcium phosphate and calcium oxalate are responsible for kidney stones. Other insoluble calcium compounds form the major components of your teeth and bones. As you can see, life really does depend on those compounds that are soluble in water, and those that are not.

Why do we find some elements, like copper or oxygen, in nature, but others, like sodium chloride, as compounds? We can imagine making sodium chloride directly from its elements, and we can watch movies of this dramatic chemical reaction on the Internet, even though we shouldn't do it at home! To write the reaction between the pure, solid metal sodium and the diatomic halogen gas chlorine, chemists place the sodium and chlorine on the left side of an arrow that points to the right and is read "forms." The word *forms* can be translated as the phrase "and a chemical reaction occurs." On the right side of the arrow the products of the reaction are written. The state of matter of the reagents and products are given by subscripts to the right of each species. The reaction between solid sodium metal and chlorine gas is then written as follows:



But this is not a completely correct summary of the reaction, because it does not illustrate the conservation of mass observed in all chemical reactions. Chemists balance chemical reactions by placing numbers in front of each reagent and product so the same number of atoms of each kind are present in both the reagents and products. In the sodium-chlorine reaction, the fact that the chlorine is diatomic means that it can form two chloride ions on the product side. Those two chloride ions require two sodium ions, but now only one is represented in the reaction. We therefore balance the reaction by placing a 2 in front of the sodium and a 2 in front of the NaCl product.



In this balanced equation the total mass of the reagents, two sodium atoms and a chlorine molecule, equals the mass of the two sodium chloride formula units.

In a small crystal of sodium chloride there are millions and millions of sodium and chloride ions. They are attracted to each other by their opposite charges. Again, the energy of the attraction is determined from Coulomb's law:

$$E \propto Q_1 Q_2 / r$$

Where  $Q_1$  is the charge on the sodium ion,  $Q_2$  is the charge on the chloride ion and  $r$  is the distance between the centers of the nuclei. The energy is called the lattice energy of the ionic solid. Coulomb's law tells us that two ions that are approximately the same size, but have charges of two instead of one, will have four times the lattice energy of their +1 neighbors. In fact, the experimental lattice energy for NaCl (787 kJ) is almost one-quarter that of MgS (3,406 kJ). The lattice energy is the amount of energy required to separate the ions from each other when 58.44 g of the salt is dissolved in water. You have to provide that much energy to overcome the attractions between the sodium and chloride ions and separate them. When the water molecules surround the ions, forming a hydration sphere, energy is released. The hydration energy for each ion also increases in proportion to the charge.

Let's consider the process of dissolution of sugar on a molecular level. You start with a sample of sugar and a sample of pure water. The sugar is a solid. The molecules of the solid are held together in small crystals by intermolecular attractive forces, and the molecules are attracted to one another. The molecules in the liquid water are also attracted to one another. In water, the attractions are called hydrogen bonds. Sugar molecules also have hydrogen bonds, but polar and dispersion forces play a role in their solid structure as well. The much larger size of the sugar compared to the water spreads the attractive forces over a larger area. For the sugar molecules to become uniformly distributed among the water molecules, the individual sugar molecules need to be separated from one another, as do some of the water molecules. To overcome the attractive forces, energy must be absorbed by the system. Chemists say the separation of molecules from one another is an endothermic process. When the molecules mix together, there must be attractive forces between the solvent and solute molecules so that intermolecular bonds are formed. When bonds are formed, energy is released from the system. Chemists call this an exothermic process. It is often convenient to illustrate the energy changes associated with a chemical process using a chart called an energy diagram. In an energy diagram, the vertical direction is a measure of the energy of the chemical system. At the appropriate place along the energy scale, horizontal lines are drawn to illustrate the energy of the chemical system. In the sugar and water system, we would draw a horizontal line to represent the initial chemical energy of the separate solid sugar and pure water components. A second horizontal line, appropriately higher up the energy scale from the first, would represent the situation when all the sugar molecules and the water molecules are separated from one another. Because the separation requires overcoming attractive chemical forces, energy flows into the system and the separated sample is at higher energy than it was initially. To actually form the solution, the solvent and solute must mix together. The mixing step is exothermic, and energy is released from the system as it happens. When the solute is soluble in the solvent, the solution's energy is lower on the scale than the energy of the separated molecules. Although in reality all of these processes, the separation of the sugar molecules from each other, the separation of the water molecules from each other, and the mixing of the sugar with the water, happen simultaneously, a mathematical treatment of

the energetics is simpler if we think of each step as independent from the other. As long as we start and end at the same chemical environment (chemists call it a state), we can think about the transformation in several different ways and gain insight about it.

Overall the process of dissolution can be either endothermic or exothermic depending on the relative amounts of energy involved in the separation and mixing steps. Because we do not conduct dissolutions in this stepwise manner (we just mix the solvent and solute together), you can conclude that actually measuring the energies associated with the steps of separating the molecules of solvent and solute and measuring the energy associated with mixing them is a very difficult undertaking. But measuring the overall energy change is not difficult at all. It is just unfortunate, for the person trying to relate chemistry to everyday life, that the amount of energy required to separate the water and sugar molecules is almost the same as the amount of energy released when a sugar solution is formed. The energetics of the system are not immediately apparent to us in our everyday lives.

The energetics when some solids dissolve in water can be much more obvious. Ammonium acetate, an ionic compound, is the active ingredient in many cold packs. The ammonium acetate is in an ampule that can easily—but not too easily—be broken. The rest of the pack is filled with water. When the ampule is broken and the ammonium acetate dissolves in the water the cold pack gets cold. The energy required to separate the ammonium ions from the acetate ions is much larger than the energy released by their solvation. The dissolution of ammonium acetate is an endothermic process.

On the other hand, if you need a hot pack, at least one commercial product uses a supersaturated solution of sodium acetate. A supersaturated solution is one that contains more dissolved material than you would expect from the solubility of the compound. Supersaturated solutions are metastable—given the opportunity, they will return to the state described by having a saturated solution in contact with its solid. Supersaturated solutions are generally prepared by mixing a large quantity of solid with water and heating the mixture until a homogeneous solution forms. If you cool sodium acetate slowly without disturbing it, it will stay dissolved in the water, forming the supersaturated solution. However, once you give the solution the opportunity to become saturated—by shaking it, or in commercial hot packs by clicking the metallic button inside the pack—the sodium acetate crystals form. The crystallization forms sodium acetate trihydrate, a crystal that contains sodium ions and acetate anions in a one-to-one ratio, but encases three water molecules per sodium ion in its solid lattice structure. The precipitation forms chemical bonds and is exothermic, providing a chemical source of heat for the hot pack. To reuse a cold pack, it needs to be opened to allow the water to evaporate. Heat packs, however, can easily be reused. You simply place the entire thing in boiling water, redissolve the sodium acetate, and leave it alone to cool off, reforming the saturated sodium acetate solution in the process.

## For Greater Understanding

### Questions

1. When potassium nitrate dissolves in water, the temperature drops. Which is correlated with a larger amount of energy, the separation of potassium and nitrate ions from each other or the solvation of the two ions by surrounding water molecules?
2. Which of the following solutions do you expect will be electrolytes and conduct electricity?
  - a. Sucrose in water
  - b. Ethanol in water
  - c. Potassium nitrate in water
3. Do you expect that a solution of ethanol in water will conduct electricity, or not?

### Suggested Reading

American Chemical Society, and Jerry A. Bell. *Chemistry: A General Chemistry Project of the American Chemical Society*. New York: W.H. Freeman, 2005.

Pauling, Linus. *General Chemistry*. New York: Dover Publications, 1988 (1970).

### Other Books of Interest

Cobb, Cathy, and Monty L. Fetterolf. *The Joy of Chemistry: The Amazing Science of Familiar Things*. Amherst, NY: Prometheus Books, 2005.

Kegley, Susan E., and Joy Andrews. *The Chemistry of Water*. Sausalito, CA: University Science Books, 1998.

## Lecture 3

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### Count Like a Chemist

The Suggested Readings for this lecture are the American Chemical Society and Jerry A. Bell's *Chemistry: A General Chemistry Project of the American Chemical Society*, chapter 2: "Aqueous Solutions and Solubility," and Linus Pauling's *General Chemistry*.

Next time you go to the grocery store, take a minute to look at the packaging on some of the products you buy. If you buy eggs, you probably pay for them by the dozen, not the pound. When you buy flour, you pay by the pound, not the quart. When you buy milk, you buy by volume. You buy gum by the stick, and aspirin by the number of tablets, but candy pieces by ounces or pounds. Could you buy gum and aspirin by the ounce or candy pieces by the number? Sure. But either for modern technical or archaic manufacturing reasons we don't count them that way at the grocery store.

Chemists use the same range of measuring techniques as grocers, but they are much more flexible about converting from mass to volume to number of items than are grocers in a modern store. The density of a substance allows us to convert from its volume to its mass and vice-versa. Now we want to relate the number of atoms or molecules in a sample to its mass. We can imagine how to do this with aspirin or eggs. We simply count out a sample and weigh it. We might repeat the measurement a couple of times and get the average result, because we know that all aspirin and all eggs are close in size and weight but are not exactly identical in mass. The big complication in chemistry is the fact that individual molecules or atoms chemists count are so small that any normal, measurable mass or volume is going to contain inconceivably huge numbers of particles. Fortunately for us, the periodic table and the chemists who developed it again come to our rescue. If you take the number at the bottom of the periodic table block and express it in units of grams, the number of atoms in the sample is always the same— $6.02 \times 10^{23}$ . In decimal notation this is 602 million trillion, or, more properly, 602 sextillion, that is, 602,000,000,000,000,000,000,000 items. Chemists define this quantity as one mole. Any collection of  $6.02 \times 10^{23}$  items is one mole of items. This is exactly the same as saying one million items is  $1 \times 10^6$  items.

Back to the periodic table for a moment. Note that one mole of sodium metal will have a mass of 22.99 g; one mole of lead has a mass of 207.19 g. Both samples contain the same number of atoms, so the individual atoms of lead must be heavier than the individual atoms of sodium. What about a mole of sodium chloride? One mole of sodium chloride salt will contain one mole of sodium ions and one mole of chloride ions. Since the sodium atoms have each given their electrons to the chlorine atoms to form the ions, the mass of one mole of sodium chloride is exactly the sum of the mass of one mole of sodium atoms and one mole of chlorine atoms:  $22.99 \text{ g} + 35.45 \text{ g} = 58.44 \text{ g}$ . What about one mole of

methane, CH<sub>4</sub>? Can you see that the mass of one mole of methane is the same as the mass of one mole of carbon atoms plus four moles of hydrogen atoms—12.01 g + (4 × 1.01 g) = 16.05 g. While you might find it annoying to hear the unit “gram” after every number here, chemists are pretty neurotic about keeping units with numbers. It helps in problem solving and avoids catastrophes like the crash of the Mars orbiter in September 1999 that resulted when scientists from NASA and engineers from Lockheed Martin failed to communicate their measuring units clearly to each other. The engineering team used English units, while NASA scientists assumed everything was in metric terms.

How big is a mole? As an illustration, we'll assume a “lifetime” is ninety years. If we wanted to count a mole of sodium atoms at one atom per second it would take 212 trillion lifetimes (212,000,000,000,000). The six thousand years of recorded human history allow for only sixty-seven ninety-year lifetimes. Think about this for a moment and you will begin to perceive how small atoms, ions, and molecules are and how many of them are in even the smallest spec of dust. You can see why chemists prefer to weigh out samples—counting them is absolutely impossible.

Now that we can appreciate how enormous a number a mole is, let's take a few moments and run through a household example of a calculation a chemist might do converting between grams and moles. The salt canister in my pantry is about half empty. Let's say it contains 292.2 g of salt. How many moles of salt are in my pantry? Just as we used the density of a substance as a conversion factor to allow us to express a quantity in either grams or liters, we use the molar mass of a substance to allow us to convert between grams and number of moles. We know that one mole of NaCl has a mass of 58.44 g. So to solve this problem, we begin with what we know and use the molar mass of the sodium chloride as the conversion factor:

$$292.2 \text{ g NaCl} \times \left( \frac{1 \text{ mole NaCl}}{58.44 \text{ NaCl}} \right) = 5.000 \text{ moles NaCl}$$

So the 292.2 g is 5.000 moles of NaCl. The zeroes after the number 5 represent “significant figures.” Since the periodic table lists the mass of sodium and chloride to four significant figures and the mass of salt in the problem is given to four significant figures, four significant figures are kept in the answer. The zeroes to the right of the decimal are significant here. The sample of NaCl contains 5.000 moles of sodium ions and 5.000 moles of chloride ions. If we wanted to count them individually, we would have  $5 \times 6.02 \times 10^{23}$  sodium ions or  $3.01 \times 10^{24}$  sodium ions. That's a lot.

Molar mass relates grams to moles, and density relates mass to volume. For instance, half a mole of ethanol is the same quantity of Methanol as 23.04 g or 29.2 cm<sup>3</sup>. Conversion factors make it possible for us to count the number of atoms, ions, or molecules in a sample, whether we know its mass or its volume. This flexibility is important in making chemistry a more practical science. Most introductory chemistry texts provide a flow chart

of conversion factors to support students in solving unit conversion problems. But it is just a graph that illustrates the technique called “dimensional analysis.”

Sometimes, chemists call one mole “Avogadro’s number.” Amedeo Avogadro was an Italian chemist who studied gases in the early 1800s. He first proposed that any volume of any gas sample contained the same number of molecules as that same volume of any other gas, as long as the temperature and pressure were the same. His hypothesis was based on a careful study of reactions between gases. Today, the mole is formally defined as the number of carbon-12 atoms in 12.011 g of carbon. As such, it is experimentally determined and subject to some uncertainty.

Let’s take a brief detour into Avogadro’s world to see the genesis of his revolutionary idea. The story starts in the 1660s. Robert Boyle and his assistant Robert Hooke set out to measure the volume of a gas sample as a function of pressure. The device they used was similar to an old mercury barometer. A “J”-shaped glass tube is closed on the short end. Mercury is poured into the tube. When the levels of the mercury on both sides of the tube are the same, the pressure exerted by the gas captured in the short end of the tube is equal to the atmospheric pressure in the room. Boyle and Hooke demonstrated that the relationship between the volume and the pressure was exactly an inverse relationship.

The next of the gas laws was discovered by French mathematician J.A.C. Charles (1746–1823). Charles is noted as one of the first people to ascend in a hot air balloon. His scientific contributions were to perform a systematic study of the volume of gas as a function of temperature. Charles determined that all gases showed a linear increase in volume with temperature. More interestingly, when his experimental data was extrapolated to determine the temperature where the gas would occupy zero volume, all the samples he investigated gave the same result. On the centigrade scale, the gas samples had zero volume at  $-273.15$  degrees. Today, you can easily see Charles’s law in action if you buy helium balloons from the party store. The balloons will undoubtedly appear fully inflated in the store. But if you are having a party on a cold day in January, you may be surprised as the balloons appear to deflate in your car on the way home. Once you get them in the house, they reinflate, so if you are a little slow, you won’t call the balloon store to complain. The deflation results from the cold temperature outside the store. The balloons reinflate as they warm back to room temperature in your house.

Avogadro followed Charles and observed that the volume of a gas increased linearly with the amount of gas. He hypothesized that equal volumes of two gases, when held at the same temperature and pressure, contain equal numbers of gas molecules.

Eventually, the three separate gas laws were combined into one overall equation, today called the ideal gas law:  $PV = nRT$ .

If you measure the pressure, volume, temperature, and number of moles of any ideal gas, the ratio  $PV/nT$  always gives the same numerical value— $R$ . Therefore,  $R$  is called a universal constant. The gas law was determined experimentally, but it opened a theoretical

window into the fundamental nature of materials by enabling development of the kinetic theory of gases. The kinetic theory and its mathematical formalism contributed to the modern picture that molecules and atoms are discrete entities in constant random motion. In addition to motivating us to count like a chemist, the kinetic theory allows us a glimpse into the chaotic, electrodynamic, and mostly unseeable world of atoms and molecules.

Let's revisit the solutions we discussed in lecture 2. When solutions are prepared in the lab, it is usually easiest to report the amount of solute and solvent in terms of the mass or volume of each component used. But solutions turn out to be trickier than one might assume. While the mass of a solution is always equal to the sum of the mass of its components, the volume of a solution is not always equal to the sum of the volumes of its components. In a macroscopic analogy, assume we decide to place some stones in a pail. We fill the pail to the top. Is the pail "full"? It is if we try to add more stones, but what if we want to add sand instead? You know that you can add the sand, shake the pail, and watch the sand fill in the spaces left between the stones. In general, the bigger the stones, the more sand you can get into the pail. When you have filled the pail with sand, is it full? Not if you try to add water! Even if the pail looks completely full of stones and sand, you know that you can add water and it will fill the small spaces between the sand particles. The total mass of the stones, sand, and water in the pail is equal to the mass of the stones added to the mass of the sand added to the mass of the water. But if you measured the volume of the stones, sand, and water independently before you mixed them, you would not find that the volume of the stones, plus the volume of the sand, plus the volume of the water equaled the volume of the pail. Chemicals work like the stones, sand, and water. When they are mixed together, they can fit into the spaces left between their partner's molecules. Volume is not additive.

In chemistry, there are two approaches to making solutions. One is used when the solute is truly a minor component in a solution. This technique is called the volumetric preparation of solutions. The other, appropriate for any solution, uses mass exclusively. It is easy to measure the volume of liquids. In your kitchen you use a measuring cup. In a lab, chemists use a variety of calibrated volumetric measuring devices, one of which is a volumetric flask. A volumetric flask is wide at the bottom but has a long, narrow neck. The manufacturer of the volumetric flask calibrates the glassware and provides a single mark on the neck of the flask indicating the position of the meniscus when a specific volume of solution is contained in the flask. The manufacturer does this by adding a specific mass of a material with a known density—for instance, water—to the flask and marking the level of its meniscus. Thereafter, anytime the flask is filled to that same level, the chemist can be confident that he or she knows the volume of the sample to within the uncertainty the manufacturer reports for the glassware. Careful medicinal, pharmaceutical, or environmental chemists often keep scrupulous historical data on their volumetric glassware, recalibrating it periodically so they know if the volume of sample it holds changes from one experiment to the next.



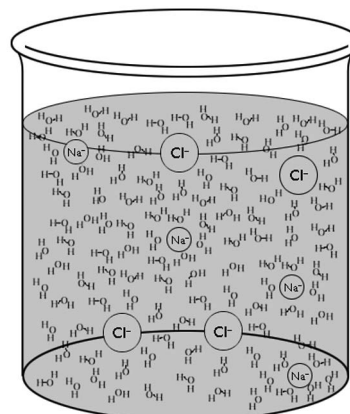
To prepare a solution of salt water, a chemist weighs out a known mass of salt, say 10.00 grams, and places it in a volumetric flask. The chemist then adds some distilled water and swirls the flask to dissolve the salt. Once the salt is dissolved, more water is added until the meniscus is exactly at the level marked on the volumetric flask (let's assume 100 mL in this case). If all the salt dissolves, we could say that the concentration of salt in water is 10.00 g/100 mL. This is a perfectly good way to report the concentration of the salt solution. Of course, it's not the only way. If we want to use this solution in a reaction, we may want to know how many sodium or chloride ions are present in the 100 mL sample, rather than the mass. To report this, we convert the 10.00 g to moles.

$$10.00 \text{ g} \times (1 \text{ mole}/58.44 \text{ g}) = 0.1711 \text{ mol sodium chloride}$$

So now we can report the concentration of the salt solution as 0.1711 moles in 100 mL. But remember that the liter is the base unit of volume. Chemists prefer to use base units when possible. If we wanted to make one liter of solution with a concentration of 0.1711 mole per 100 mL, we would need ten times more moles of NaCl and ten times the total volume—remember that 1,000 mL is equal to 1 L. So if we want to prepare one liter of a solution with a concentration of 0.1711 moles in 100 mL, we need 1.711 moles of salt and enough water to prepare 1.0 liter of solution. The concentration of the larger volume would be reported as 1.711 mole per liter. The concentration unit using the liter standard volume gets a special name, Molar. The solution we have prepared by dissolving 1.711 moles of NaCl in enough water to make 1.00 L of solution has a concentration of 1.711 Molar. Lazy chemists write 1.711 M. Remember, this is exactly the same concentration as the solution reported as being 0.1711 mole/100 mL; there is just more of it. So the same solution can be said to have a concentration of 10.00 g NaCl/100 mL, or 0.1711 mol/100 mL or 1.711 M. They are all different names for the exact same concentration. The unit we use depends on the problem we are trying to solve and personal preference. As long as we can all interconvert between units, we can understand each other. That is the goal.

Chemists call the solution preparation strategy described above “dissolve and dilute.” They always completely dissolve the solute before adding solvent to the final volume because dissolution can change the volume of the solution when compared to the sum of the volumes of the solute and the solvent. When volumetric concentrations are used, this can be a significant source of error in lab work or in calculations.

Once we know the molar concentration of a solution, we can easily use volumetric measurements to obtain any quantity of solute we want. For example, if we measure out 50.00 mL of the 1.711 M NaCl solution on the shelf, we will have the following:



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#### Aqueous Salt (NaCl) Solution

The sizes of sodium and chloride ions are exaggerated in this drawing.

\*Note H end of water nearest  $\text{Cl}^{-1}$  and O side of water nearest  $\text{Na}^{+1}$

$$50.00 \text{ mL} \times (1.711 \text{ mol/L}) \times (1 \text{ L}/1,000 \text{ mL}) = 0.08555 \text{ mol NaCl}$$

Since multiplication is commutative, we can multiply the factors in any order and get the same answer.

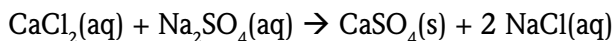
$$50.00 \text{ mL} \times (1 \text{ L}/1,000 \text{ mL}) \times (1.711 \text{ mol/L}) = 0.08555 \text{ mol NaCl}$$

If we know we want 6.00 g of NaCl, we can determine the volume of the solution needed, too, using the concentration, 1.711 M solution, as a conversion factor:

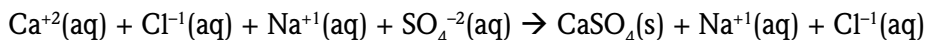
$$6.00 \text{ g} \times (1 \text{ mol}/58.44 \text{ g}) \times (1 \text{ L}/1.711 \text{ mol}) = 0.0600 \text{ L or } 60.0 \text{ mL}$$

The problem-solving method used here employs concentrations in the same way as densities, as conversion factors. The units you have and the units you want determine whether the conversion factor is used right side up or upside down.

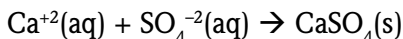
In the previous lesson, we discussed the precipitation of calcium sulfate from mixing together solutions of calcium chloride and sodium sulfate. Let's revisit the reaction and consider it in more detail. The balanced chemical equation for the reaction can be written in several ways. The first includes all the information available.



Note a few things in this total equation. The subscripts identify the precipitate and the NaCl needs a two in front to account for all the sodium and chloride ions provided by the original solutions. This reaction reflects the procedure we are conducting in the lab, but it does not do a very good job of illustrating the chemistry that is happening when the precipitate is formed. In reality, all species present before the reaction is initiated are better described as independent solvated ions in solution, as are the Na and Cl ion in the product. It is perhaps more helpful to write the reaction in a form called a complete ionic equation.



This form shows all the species in their correct states before and after the reaction, but it does not reflect that the chloride is actually present in twice the concentration as the calcium. The complete or total ionic equation form also requires that we write both the sodium and the chloride ions the same on both sides of the arrow. While this emphasizes that they do not participate in the reaction, it is something that a chemist focused on the chemistry of the reaction would really prefer to avoid. In the case where the reaction is the most important feature, the net ionic equation is the most concise way of conveying information. The net ionic equation only shows chemical species that undergo a change in the course of the reaction. Here the net ionic equation is as follows:



Note that the net ionic equation completely ignores the spectator ions, providing only information about the species that actually undergo a transformation when the solutions are mixed. The stoichiometry of the reaction allows us to determine how much solution we need, or how much product we will form.

Let's consider some kitchen stoichiometry for a moment, before we examine solution stoichiometry. An old recipe I have for a pound cake calls for a pound of flour, a pound of sugar, a pound of eggs, and a pound of butter. The stoichiometry is pretty straightforward. If you have a pound of flour, a pound of sugar, a pound of eggs, and a pound of butter, you can make a pound cake. If you only have a half pound of sugar, you can't make a complete pound cake. But you could make a half-sized pound cake, using only half a pound of your flour, half a pound of eggs, and half a pound of butter. You would make half a pound cake. Sometimes, that might be enough—or it might be the best you can do. Chemical stoichiometry is exactly like baking stoichiometry. In baking, the recipe tells you the ratio of the amount of each ingredient you need to use. If you are short an ingredient, you can reduce all the ingredients by half, and usually things still work out fine. You just make half the product the recipe indicates. Or, if you have lots of folks coming, you can double the recipe and make two pound cakes. In chemistry, a balanced reaction takes the place of a recipe. The balanced reaction tells you the number of each kind of reagent you need, and the number of products you form. It can be read as referring to individual molecules or formula units, or moles of molecules or formula units. So in the precipitation reaction we just discussed, the net ionic equation  $\text{Ca}^{+2}(\text{aq}) + \text{SO}_4^{-2}(\text{aq}) \rightarrow \text{CaSO}_4(\text{s})$  can be read as follows: one calcium +2 ion and one sulfate -2 ion combine to make one  $\text{CaSO}_4$ ; or 100,000 calcium ions and 100,000 sulfate ions make 100,000 calcium sulfate formula units *or* one mole of calcium ions plus one mole of sulfate ions make one mole of calcium sulfate. This precipitation is said to have 1:1 stoichiometry. If you only have 0.20 moles of calcium ions, you can't make 1 mole of calcium sulfate, but you can mix your 0.20 moles of calcium ions with 0.20 moles of sulfate ions to precipitate 0.20 moles of calcium sulfate. What would happen if you mixed a solution containing 0.20 moles of calcium ion with a solution containing 0.30 moles of sulfate ions? You would run out of calcium ions before you used up the sulfate ions. The calcium ion would be considered the limiting reagent in this reaction. It would place a limit on the amount of product that could be made. From this mixture you would make 0.20 moles of calcium sulfate, leaving 0.10 moles of excess sulfate behind in the solution. That's really all there is to chemical stoichiometry.

But, of course, life is always more complicated, isn't it? Let's consider the solution stoichiometry we would really face in a lab environment. Two exceptions to the "chlorides are soluble" rule are silver (I) chloride,  $\text{AgCl}$ , and lead (II) chloride,  $\text{PbCl}_2$ . Let's say we are trying to get all the metals out of some water samples. We have 50.0 mL of a solution containing 0.020 M silver (I) nitrate and 50.0 mL of another solution containing 0.020 M lead (II) nitrate. We also have a bottle of 0.100 M sodium chloride solution. How much sodium chloride solution do we need to add to the silver nitrate solution to precipitate all the silver? Even if you can intuit the answer here, it is helpful to illustrate the solution using a systematic approach.

First, write the net ionic equation for the reaction that occurs:  $\text{Ag}^{+1}(\text{aq}) + \text{Cl}^{-1}(\text{aq}) \rightarrow \text{AgCl}(\text{s})$ . This has 1:1 stoichiometry. If we figure out how many moles of silver are in our

sample, we need the same number of moles of chloride ion. Since both of the reagents are present in solution, we will need to convert from moles to volume using the solution concentrations as the conversion factor.

$$\begin{aligned}
 50.0 \text{ mL of } 0.020 \text{ M AgNO}_3(\text{aq}) &\Rightarrow 50.0 \text{ mL} \times (1\text{L}/1,000 \text{ mL}) \times \\
 &(0.020 \text{ mol AgNO}_3/1 \text{ L}) \times (1 \text{ mol Ag}^+/1 \text{ mole AgNO}_3) \\
 &= .0010 \text{ mole silver ions present} \\
 0.0010 \text{ mole of silver ions} &\times (1 \text{ mole Cl}^-/1 \text{ mole Ag}^+) \\
 &= 0.0010 \text{ mole chloride ions required} \\
 0.0010 \text{ moles chloride ions} &\times (1\text{L}/.100 \text{ moles}) \\
 &= 0.010 \text{ liters} = 10 \text{ mL chloride solution required}
 \end{aligned}$$

So we get a stoichiometric mixture of chloride to precipitate all the silver by mixing 10 mL of the 0.100 M sodium chloride solution with 50.0 mL of 0.020 M silver nitrate solution and produce 0.001 mole of silver chloride precipitate. We can add more sodium chloride solution if we want, but no more silver chloride will precipitate, once we run out of silver. This 0.001 mole of silver chloride will have a mass of

$$0.01 \text{ mole} \times (143.32 \text{ g AgCl}/1 \text{ mole AgCl}) = 0.143 \text{ g AgCl solid.}$$

Chemists generally separate precipitates from the remaining solution by running the whole mixture through a filter paper. The filter paper collects the solid but lets the supernatant solution and the ions it contains through, pretty much like a coffee filter holds the coffee grounds, while the solution drips through to the pot.

What about the 50.0 mL of 0.020 M lead (II) nitrate? How can we get the lead out of that solution? Let's follow the same procedure. The net ionic equation for the reaction is  $\text{Pb}^{+2} + 2 \text{Cl}^- \rightarrow \text{PbCl}_2(\text{s})$ . This does not have a 1:1 stoichiometry. In fact, it says we need two chlorides for every lead. This isn't any different than needing two wheels for each bicycle, or two pieces of bread for every sandwich. And the steps required to answer the question "How much sodium chloride is needed to precipitate all the lead?" are exactly the same as the steps in answering the silver precipitation question. Let's start. First, how many moles of lead ions are present?

$$\begin{aligned}
 50.0 \text{ mL} \times 0.020 \text{ M Pb(NO}_3)_2 &\times (1 \text{ mole Pb}^{+2}/1 \text{ mole Pb(NO}_3)_2) \\
 &= 0.0010 \text{ mole lead ions present} \\
 0.0010 \text{ mole of lead ions } 1.711 &\times (2 \text{ mole Cl}^-/1 \text{ mole Pb}^{+2}) \\
 &= 0.0020 \text{ moles chloride ions required} \\
 0.0020 \text{ moles chloride ions } 1.711 &\times (1\text{L}/0.100 \text{ moles}) \\
 &= 0.020 \text{ liters} = 20 \text{ mL chloride solution required}
 \end{aligned}$$

Not surprisingly, we need twice as much chloride to precipitate the lead because of the 2:1 stoichiometry. But we still make the same number of moles of product, 0.0010 moles. The 0.0010 moles of lead (II) chloride precipitated will have a mass of

$$0.0010 \text{ moles} \times (278.09 \text{ g PbCl}_2/1 \text{ mole PbCl}_2) = 0.278 \text{ g of PbCl}_2(\text{s}) \text{ will precipitate.}$$

These general steps will allow you to solve any problem in solution stoichiometry in a principles of chemistry course. It doesn't matter if you are working on the 0.100 g scale, as these problems illustrate, or whether you are dealing with tons of reagents; the structure of the calculations is the same.

Let's change our focus and look at some solutions made by dissolving gases in water. We know that fish have gills and breathe oxygen dissolved in water, just as we breathe the oxygen dispersed in our atmosphere. If you consider the solubility rules we have discussed so far, you might predict that oxygen, a nonpolar, homonuclear diatomic gas molecule, is not at all soluble in water. Obviously, the existence of fish overrules your conclusion. But please don't ignore the solubility rules we have established so far, nor the solubility principles that underlie them. Let's examine five gases in detail. We will look at their Lewis structures, predict their solubility, and compare the predictions with experimentally determined values to see if we can reconcile the discrepancy. Let's consider oxygen gas, nitrogen gas, carbon dioxide gas, ammonia gas, and hydrochloric acid gas. Oxygen, nitrogen, and carbon dioxide are major components in our atmosphere. Ammonia and hydrochloric acid are two of the most important industrial chemicals.

First, draw their Lewis diagrams and predict their solubility based on the intermolecular forces they experience. Your drawings will show that  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{CO}_2$  are all nonpolar molecules. The prediction would be that they are not soluble in water. On the other hand, ammonia,  $\text{NH}_3$ , is polar and has hydrogen bonds. It should be very soluble in water.  $\text{HCl}$  is also highly polar, but it cannot form hydrogen bonds, so you might predict that it should be less soluble than ammonia. What do the experimental results show? In order to compare apples to apples, we need to be a little careful about how we set up the experiments to make these measurements. If we take a water sample and purge all the air from the space above it so that we can expose the water to an atmosphere that contains pure nitrogen, or pure oxygen, or pure ammonia, and if we keep the pressure of the gas above the water the same, say at normal atmospheric pressure, one atmosphere, and we keep the temperature the same, say room temperature,  $25^\circ\text{C}$ , then we can get some significant results. We report the solubility of the gases in grams of gas per kilogram of water. Nitrogen and oxygen gas have measured solubilities of 0.018 and 0.039 grams per kilogram of water, respectively. Ammonia and hydrochloric acid have solubilities of 470 and 695 g per kg of water, respectively. When we look at the measured solubilities, it is clear that the predictions we made based on the structures of the molecules are aligned with the results. The compounds we predicted would be soluble dissolve hundreds of grams in aqueous solution. The compounds we said were insoluble only dissolve milligrams into solution. It turns out that a more sophisticated analysis of the solubilities of alcohols and salts in water requires us to modify our initial adamant description of nonpolar molecules as insoluble. Mother Nature is more sophisticated than that. The "rules" we developed from macroscopic observations apply to macroscopic quantities. But nature is often subtle and not interested in our absolutist pronouncements. A more sophisticated view of solubility is not that compounds

divide into two camps—the soluble and the insoluble—but that they are arrayed along a continuum. Some are miscible, some are very soluble, and some are slightly soluble. In water, the universal solvent, almost no compounds are completely insoluble. If the small solubility of oxygen in water is sufficient to support all the fish life on the Earth, you can imagine the miracles and headaches caused by the presence of other, equally insoluble compounds in our aquatic world. You might note that I skipped the solubility of CO<sub>2</sub> gas. The solubility of CO<sub>2</sub> gas illustrates the continuum of solubility, with a twist. Following our rules, you would predict that CO<sub>2</sub> should have a solubility of no more than about .100 g/kg water. In fact, the solubility of CO<sub>2</sub> is more than ten times this amount: 1.45 g of CO<sub>2</sub> will dissolve in a kg of water at 25°C.

This seems a little out of line with other nonpolar substances we have considered so far. If we examine the situation further, we find that the CO<sub>2</sub> solution we have prepared has some distinctive physical properties different from those of the nitrogen- or oxygen-saturated water. In particular, if we test the conductivity of the three gas-containing solutions, both oxygen and nitrogen produce nonconducting solutions. But carbon dioxide forms a slightly conducting solution, not equal to the conductance of salt in water, but not zero either. There must be some ions in a carbon dioxide solution. Where do they come from? If we employ a pH meter, we see that in contrast to the oxygen- and nitrogen-containing waters, the carbon dioxide- and HCl-containing waters are acidic. The ammonia-containing water is basic. We will examine the chemical reactions that must accompany the dissolution of carbon dioxide, hydrochloric acid, and ammonia in water in lecture 7.

Let's draw our introduction to counting like a chemist to a close with one more concentration conversion. We have reported the solubility of gases in water in terms of the grams of each gas that dissolves per kilogram of water. How do we determine the concentration of the gases in saturated solutions in units of moles/L? We will need two conversion factors—the first is the molar mass of the solute gas. Easy enough. The second conversion factor will have to give us the volume of the solution. That requires the density of the solution. Pay careful attention here. We need the density of the solution, which relates the mass of the solution to the volume of the solution. The mass of the solution is the total mass of both the solvent-water and the solute. In the case of oxygen, 0.039 grams dissolve in 1 kg of water, and we assume the density has not changed because of the small amount of solute. In one step, then, the molar concentration of oxygen in a saturated solution is as follows:

$$\frac{0.039 \text{ g O}_2}{1,000.039 \text{ g solution}} \times \left( \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \right) \times \left( \frac{1 \text{ g solution}}{1 \text{ mL solution}} \right) \times \left( \frac{1,000 \text{ mL}}{\text{L}} \right) = 1.2 \times 10^{-3} \text{ M}$$

## For Greater Understanding

### Questions

1. What is the mass of 0.500 moles of dry ice,  $\text{CO}_2(\text{s})$ ?  
a. 44.0 g                      b. 22.0 g                      c. 88.0 g                      d. 56.0 g                      e. 28.0 g
2. What mass of  $\text{CaCl}_2$  is needed to prepare 200 mL of a 1.00 M solution of calcium chloride?  
a. 111.0 g                      b. 55.5 g                      c. 22.2 g                      d. 222.2 g                      e. 555.5 g
3. Use the solubility of oxygen reported above to calculate the mass of oxygen gas dissolved in a tank of water that holds 5,000 gallons of water. Remember that 1 gallon = 3.785 L and assume that the density of oxygenated water is 1.00 g/mL.  
a. 605,000 g                      b. 160,000 g                      c. 18,925 g                      d. 727 g                      e. 22.7 g

### Suggested Reading

American Chemical Society, and Jerry A. Bell. *Chemistry: A General Chemistry Project of the American Chemical Society*. New York: W.H. Freeman, 2005.

Pauling, Linus. *General Chemistry*. New York: Dover Publications, 1988 (1970).

### Other Books of Interest

Henrickson, Charles. Chapter 5: "The Mole—Elements and Compounds" and chapter 13: "Solutions and Solution Concentrations." *CliffsStudySolver Chemistry*. Hoboken, NJ: Wiley Publishing, Inc., 2005.

Rosenberg, Jerome L., Lawrence Epstein, and Peter J. Krieger. Chapter 12: "Concentration of Solutions." *Schaum's Outline of College Chemistry*. 9th ed. New York: McGraw-Hill Companies, Inc., 1997.

## Lecture 4

### The Origin of Atoms

The Suggested Reading for this lecture is the American Chemical Society and Jerry A. Bell's *Chemistry: A General Chemistry Project of the American Chemical Society*, chapter 3: "Origin of Atoms."

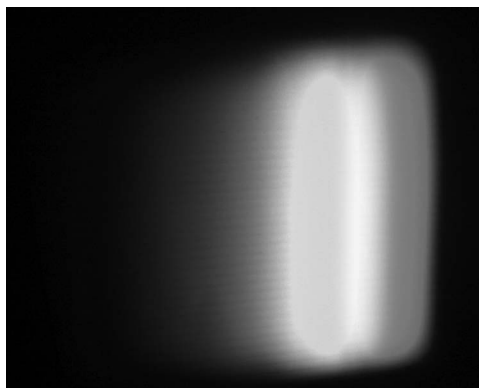
Rainbows are transient manifestations of water's ability to diffract light from our sun. Newton is widely credited with first "observing" that white light, pretty similar to the light from our sun, could be dispersed into the colors of light observed in a rainbow. Newton made this discovery by passing solar light through a prism. Most probably, he was not the first to see this non-rainbow. But he was the first to observe, in 1672, that the spectrum recombined to give back the white light he started with when the bow of colored light was passed through a second prism. Today, scientists call the rainbow of light formed when sunlight passes through raindrops, a prism, or through a grating, a *spectrum*. The visible spectrum stretches from red through violet-colored light.

Newton clarified the idea that the white light was composed of the separate colors of visible light. He then took a monochromatic component, one color, from the spectrum generated by one prism and passed it through a second prism, establishing that no further colors were generated. That is, light of a single color did not change color on refraction. He concluded that white light was made up of all the colors of the rainbow, and that on passing through a prism, these different colors were refracted through slightly different angles, thus separating them into the observed spectrum.

In 1752, the Scottish physicist Thomas Melvill discovered that putting different substances in flames, and passing the light through a prism, gave differently patterned spectra. Ordinary table salt, for example, generated a "bright yellow" light. Not only could the color be seen by the naked eye, but when the light was passed through a prism, only the yellow light appeared—the rest of the colors of the rainbow were missing. Each different substance seemed to have its own identifiable pattern; in all there were dark gaps in the spectra, and for many materials there were just a few patches of light.

Refracted Rainbow

Using a good dispersion prism, a low-wattage compact projector lamp, and a power supply, a strong, bright display of the refracted rainbow coming from an incandescent light source can be made.



© Lighting Sciences Canada, Ltd.



Eventually, it occurred to scientists to ask if there was anything “outside” the visible spectrum. Astronomer William Herschel (1738–1822) investigated this question and published his results in 1800. Herschel used a prism to refract light from the sun and placed a thermometer against the wall in a location just beyond the red end of his projected spectrum. He carefully recorded the temperature increase and reported the discovery of infrared radiation. Even in Herschel’s time people were certainly aware of the warmth provided by basking in the sun, a primary consequence of the interaction of the invisible infrared light with our material world.

A year after Herschel’s report, Johann Ritter reported the discovery of invisible light at the other end of the spectrum. Ritter used silver chloride in his experiments. He knew that silver chloride turned from violet-white to black when exposed to sunlight. Ritter measured the rate at which silver chloride reacted when exposed to the different colors of light. He demonstrated that blue and violet light caused silver chloride to turn black more quickly than red light did. He then placed silver chloride in the dark region just past the violet end of the spectrum. The silver chloride turned black. Ritter concluded that an invisible kind of light existed past the violet end of the spectrum—this is now called “ultraviolet” light.

By 1802, William Wollaston (1659–1724) in England had discovered that the solar spectrum was not really continuous. It had dark lines interspersed in the rainbow of colors. German optician Joseph von Fraunhofer undertook a systematic study of the dark lines beginning in 1814. He used multiple prisms to spread the solar radiation out in broader and broader spectra. He found an “almost countless number” of dark lines in the solar spectrum and developed an identification method for the dark lines still used by astronomers today. He labeled the strongest dark lines A, B, C, D, and so on.

By the 1820s, Herschel had recognized that Melvill’s flame spectra provided a way to detect and identify small quantities of an element in the lab by putting the element’s powder into a flame.

In 1849, Léon Foucault (1819–1868) used the technological advances of the age and examined the spectrum of light emitted when a voltaic arc was sent between two carbon poles. In his laboratory-generated lightning, he saw a bright double yellow line at exactly the same wavelength as Fraunhofer’s dark D line in the solar spectrum. Investigating further, Foucault passed the sun’s light through the arc, then through a prism. He observed that the D lines in the spectrum were even darker than usual. After testing with other sources, he concluded that the arc, which *emitted* light at the D line frequency, would also *absorb* light from another source at that frequency.









Today, we use discharge tubes filled with low-pressure gases to generate the line spectra of the gaseous elements on the periodic table for study in the laboratory. The predictable patterns of light absorbed and emitted by the elements allow sophisticated analysis of trace amounts of materials using techniques such as atomic absorption spectroscopy or inductively coupled plasma spectroscopy.

Astronomers use the line spectra of atoms to identify the elemental composition of distant stars. The relative brightness of the elements gives a clue as to their relative abundances. Although the analysis is quite sophisticated, current data shows that hydrogen is the most abundant element in the universe, with helium a distant second. The abundance of heavier elements, in general, decreases as the atomic number increases. However, the elements with even atomic numbers are more abundant than those with odd atomic numbers. Iron and its elemental neighbors defy the general trend and are unusually abundant, with iron the third most abundant element after hydrogen and helium.

Chemists, physicists, geologists, and astronomers are all interested in explaining why the universe contains the elements that it does. In order to understand their arguments, we need to review the structure of the atoms. You probably know that atoms are composed of three subatomic particles—protons, neutrons, and electrons. The protons carry a unit charge of +1 and have a mass of approximately 1 atomic mass unit (amu). The neutrons, which occupy the nucleus with the protons, are uncharged, neutral, and only slightly more massive than protons. For our purposes we will consider them to also have a mass of 1 amu. Electrons have a unit charge of −1 but are only about 1/1,800th as massive as the proton. Therefore, they contribute very little to the total mass of an atom.

The number of protons in the nucleus identifies the element and is called the *atomic number* of the element. Atomic numbers are represented by the letter Z. The elements on the periodic table are organized in order of increasing atomic number, which is the integer usually shown at the top of each block on the periodic table. Physicists interested in nuclear transformations sometimes write the atomic number as a subscript to the left of an element's symbol, but chemists consider this redundant and determine the atomic number from the element's symbol. They know He is 2, carbon is 6, iron is 26, and so on.

In addition to protons, all elements but normal hydrogen have neutrons in their nuclei. Since protons and neutrons have approximately the same mass, the mass number, represented by the letter A, is equal to the total number of protons and neutrons in an element. The mass number represents the approximate mass of an atom in atomic mass units. Mass numbers are represented by superscripts to the left of the chemical symbol. Two atoms of the same element must contain the same number of protons but may have different numbers of neutrons. The two are then called *isotopes*. Carbon-12 is the most common isotope of carbon, but carbon-13 occurs in nature, too.

TEN MOST COMMON ELEMENTS IN THE MILKY WAY GALAXY		
Atomic Number	Element	Mass Fraction in Parts Per Million (ppm)
1	Hydrogen	739,000 (71 times mass of Oxygen [red bar])
2	Helium	240,000 (23 times mass of Oxygen [red bar])
8	Oxygen	10,400 
6	Carbon	4,600 
10	Neon	1,340 
26	Iron	1,090 
7	Nitrogen	960 
14	Silicon	650 
12	Magnesium	580 
16	Sulfur	440 

Source: Croswell, Ken. *Alchemy of the Heavens*. New York: Anchor, 1996.

The nucleus of an atom of carbon-12 contains six protons and six neutrons, whereas the nucleus of an atom of carbon-13 contains six protons and seven neutrons.

Electrically neutral atoms must contain equal numbers of protons and electrons, so a neutral carbon-12 contains six electrons, as does a neutral carbon-13 atom. A lot of chemistry involves atoms trading electrons to form ions. When this happens, the excess charge is written as a superscript to the right of the element's name. So a sodium atom with twelve neutrons, but only ten electrons, is written as follows:

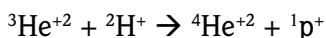
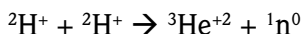


Nuclear reactions involve what the medieval alchemists called “transmutation”—one element is converted to another. Nuclei undergo transformation by absorbing and/or emitting particles. You have probably heard of alpha and beta particles. Alpha particles are helium nuclei—two protons and two neutrons. It is easy to understand how they can be emitted from nuclei. Beta particles are electrons.

How do nuclei, consisting of protons and neutrons, emit electrons? Neutrons aren't as fundamental, or as permanent, as we might hope. They can decay, forming a proton, an electron, and a third product, not of interest in most of chemistry, but called an electron antineutrino. When a neutron converts into an electron, proton, and an antineutrino, the proton is captured in the nucleus, the emitted electron is called a beta particle, and the antineutrino is really hard to detect—so chemists usually ignore it.

Some nuclear processes don't produce particles, just energy. The energy emissions are called gamma rays. Emitting a gamma ray does not change the chemical nature of a nucleus. But due to the law of conservation of energy, it produces a less energetic nucleus.

Just as mass is conserved in chemical reactions, charge, mass number, and atomic number are conserved in nuclear reactions. So now we are back to the question that began this lecture—what is the origin of atoms? Today, the commonly accepted scientific model for the formation of the universe is the big bang theory. This theory asserts that the universe began in what mathematicians would label a singularity, an initial state of unimaginably high mass, density, and temperature from which the universe began expanding about  $10^{10}$  years ago. As the primordial soup expanded, it cooled and its particles began to stick together. After a few seconds, the temperature dropped enough (although it was still hotter than any environment that can be produced) so that protons and neutrons began to stick together and form hydrogen, helium, and lithium nuclei. The reactions that allowed these nuclei to form are called *fusion* reactions—where heavier products are formed from the combination of usually two lighter particles.



At the incredibly high temperatures following the big bang, the helium (He) and hydrogen (H) nuclei had sufficient kinetic energy to overcome the Coulombic repulsion caused by them both having positive charges. Fairly quickly, however, the expanding universe cooled, reducing the kinetic energy of the nuclei and effectively bringing a halt to these nuclear fusions. Eventually, the universe cooled sufficiently for the nuclei to capture and hold onto electrons, allowing them to become neutral atoms. Today, the universe contains vast clouds of hydrogen and helium, remnants of the big bang.

So if the big bang cooled off when everything was still hydrogen and helium, where did the rest of the elements come from? All the elements came from stars. As the vast clouds of hydrogen and helium began to cool, gravity took over and began to cause local increases in density and temperature. In these regions, as gravity drew atoms closer together, the process of nuclear fusion began again. Virtually all fusion reactions release energy, contributing to further heating and facilitating increased fusion events. As the fusion processes reduced the number of particles in stars, they collapsed, much like a balloon collapses when air is removed from it. Continuing cycles of fusion, heating, and collapsing have produced all the naturally occurring elements in the universe, up to element 92—uranium.

Using fusion cycles similar to the ones discussed here, one would predict that the higher the atomic number, the less abundant the element in the universe. Is this prediction true? And how do we determine the abundance of elements in the universe anyway?

In general, the abundance of the elements decreases as the atomic mass increases. However, there are three important exceptions to this general trend. The elements lithium, boron, and beryllium are much less abundant than their neighbors. Second, iron is more abundant than its neighbors, and third, elements with even atomic numbers are consistently ten times more abundant than their odd-atomic-number neighbors.

Spectroscopy is the method by which astronomers analyze light arriving at Earth from distant stars and violent astronomical events. Wavelengths of light that are captured are compared to the wavelengths of light observed by atomic absorption or emission studies in the lab to identify which elements are present where. The relative intensity of the light provides information about the abundance of each specific element.

In addition to optical spectroscopy, it is also sometimes possible to detect and analyze the energy of particles emitted as products in nuclear reactions. We are most familiar with alpha, beta, neutron, and gamma rays, all of which can be emitted from nuclear reactions. But more exotic particles—positrons and neutrinos, for example, can also be produced.

Nuclear reactions follow conservation laws, just like chemical reactions. In nuclear processes, the total mass number, total atomic number, and total charge must be the same for the reagents and the products. But just because a nuclear reaction follows the rules, it does not mean that it produces a stable product. In fact, many products of nuclear reactions are themselves unstable and spontaneously undergo other nuclear decay processes on a

time scale characterized by a half-life. In fact, the spontaneous decay of uranium, observed by Henri Becquerel in 1896, allowed him to report the discovery of “radioactivity.”

Coulomb’s law predicts that nuclei with more than one proton should instantly self-destruct. Multiple nuclear forces come into play in nuclei, however, and allow some nuclei to be stable. The nuclei that are not stable undergo reactions called nuclear decays on time scales ranging from microseconds to millions of years. The most common stable nuclei in living systems on Earth include hydrogen-1 and hydrogen-2, which is given the special name deuterium; carbon-12 and carbon-13; nitrogen-14 and nitrogen-15; and oxygen-16, oxygen-17, and oxygen-18. In each of these examples, the lowest mass number isotope accounts for more than 99.5 percent of naturally occurring atoms.

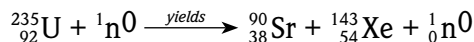
How do we determine the stability of nuclei? You might note an interesting omission from the list of quantities conserved in nuclear reactions—mass. In fact, if you compare the total mass of the individual protons and neutrons that make up any nucleus to the mass of the nucleus itself, you will find that the nucleus—except for  $^1\text{H}$ —always weighs less than the sum of its parts. This mass defect would be released as energy if you built a nucleus in one step from its component protons and neutrons. However, even when the nuclei are built in a stepwise fashion, the mass defect of the products when compared to the reagents is released as energy from the nuclear reaction. The amount of energy released is calculated according to Einstein’s famous equation  $E=mc^2$  (energy equals the mass defect times the speed of light squared). The mass difference between the nucleus and the sum of its parts is called the binding energy of the nucleus. The larger the binding energy per nucleon, the more stable the nucleus.

Let’s note that our friend, the periodic table, lists the average mass of the atoms of each element according to their relative abundance on Earth, not the mass of individual nuclei. The mass of individual nuclei is compiled in tables of the nucleons. Since hydrogen-1 has only one proton in its nucleus, its binding energy is zero. Despite being the most abundant element in the universe, on this technicality, it might be considered the least stable. The most stable element is iron-56. It has the largest binding energy per nucleon of any nucleus. The stellar fusion reactions we have discussed as important in the formation of the universe can now be reexamined from the standpoint of the energies of their reagents and products. In these cases, as elements with large atomic numbers are formed from the fusion of smaller nuclei, the binding energy per nucleon in the product is larger than the binding energy per nucleon in the reagents.

For nuclei larger than iron, however, the situation is different. Large nuclei release less binding energy per nucleon than iron-56, when formed from protons and neutrons, and are less stable. They are therefore prone to a different type of nuclear reaction—spontaneous nuclear *fission*. During fission, a large nucleus splits into two or more smaller nuclei, emitting the excess binding energy in the process. Uranium-235 undergoes a fission reaction that produces strontium-90, xenon-143, and two neutrons with a half-life of about 713,000,000 years. The reaction also releases  $7.0 \times 10^7$  kJ of energy per gram of U-235

that decays. To put this in perspective, the methane that is burned in a gas stove or gas furnace produces about 56 kJ per gram.

It is also possible to induce a nuclear fission process by hitting a large nucleus with a neutron. The same fission process that occurs naturally in U-235 can be promoted by hitting it with a neutron.



Note that the net reaction here is identical to the natural fission reaction above. The energy released is the same as the natural reaction, too. The three neutrons formed as products here illustrate that this spontaneous fission can undergo a chain reaction. If there is enough  $\text{U}^{235}$  around, the three neutrons produced by the first fission can promote three more fissions, and those fissions can promote nine more, and so on, expanding with geometric precision the impact of this otherwise slow spontaneous process.

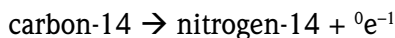
How does the binding energy per nucleon affect the abundances of the elements? If you consult a chart of binding energies, you will note that lithium, beryllium, and boron have unusually low binding energies. They are not very stable. There is less energy released when they are formed by fusion. And they are more likely to undergo spontaneous fusion processes that transform them into heavier elements. So it is not too surprising that they are less abundant in the universe than their neighboring elements.

The higher abundance of even-atomic-number elements compared to their odd-numbered neighbors is also explained by balancing competing rates of formation and decay. Recall that the first step in stellar evolution is accompanied by a depletion of the hydrogen that fuses to form helium. The higher-atomic-number elements are therefore more likely to form by fusion of even-atomic-numbered species. The binding energy of these even-numbered species combines with the environment to determine whether the even species undergo reactions forming odd-numbered nuclei. The importance of helium in stellar evolution supports the higher relative abundance of the even-atomic-numbered nuclei.

It is important to note that stellar evolution is continuing to happen today. The spectacular pictures from the Hubble space telescope not only impress us with their beauty, they provide new data for astronomers, physicists, chemists, and geologists to examine to continuously refine our understanding of our universe. In 2012, we can expect to see equally impressive pictures from completely different spectra as NASA releases data from its Wide-field Infrared Survey Explorer (WISE) satellite, which has been studying invisible infrared radiation from across the universe since its launch in 2009.

Today, we make use of naturally occurring radioactivity in a number of ways. Since its discovery by Henri Becquerel (1852–1908) in 1896, radioactivity has been employed to examine the age of archaeological items and the Earth itself. Radioactivity has found a variety of applications in medicine, has been used to generate power, and has been loosed with terrible fury in acts of war.

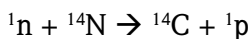
The lifetime of a radioactive process is one factor important in determining its utility. A half-life is the period of time it takes for half of the nuclei in a sample to undergo a specific nuclear process. It turns out that this time is always completely independent of the amount of radioactive material present when we start to observe the process. For example, carbon-14, carbon with six protons and eight neutrons in its nucleus, undergoes beta decay with a half-life of  $5,730 \pm 40$  years. The decay reaction is as follows:



If we have a collection of 1,000 carbon-14 nuclei, the half-life tells us that 5,730 years from now, if we come back and examine the same collection of nuclei, half of them, 500, will be carbon-14, and half of them, 500, will be nitrogen-14. After another 5,730 years, or 11,460 years after we first began our study, half of the remaining carbon-14's, or 250 carbon-14's, will remain, the rest will have decayed to nitrogen-14. Mathematically, we can calculate the fraction of the original nuclei remaining after any number of half-lives as follows (where  $n$  is the number of half-lives):

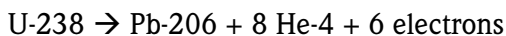
$$f_n = \frac{N_n}{N_0} = \left(\frac{1}{2}\right)^n$$

Of course we can't date archaeological items by comparing the number of carbon-14 nuclei present today to the number present when they were made, because we don't know the number of carbon-14 nuclei present when they were made, or do we? It turns out that, within some uncertainties, we do know how much carbon-14 was present when some archaeological items were made. That's because the primary source of carbon-14 on the earth is from the reaction of nitrogen-14, the major component of our atmosphere, with high-energy cosmic rays that provide neutrons to promote the reaction:



Although the baseline has been refined over time, we will simplify the argument here. Assume the rate at which cosmic rays have been hitting our atmosphere is constant over the history of man. The rate of natural decay of carbon-14 is also constant. Therefore, over time a constant amount of carbon-14 has been present in our atmosphere. Because plants take atmospheric carbon dioxide and recycle carbon-containing wastes, the amount of carbon-14 in living things matches the amount of carbon-14 in our atmosphere. But when the living thing dies, it stops exchanging carbon-14 with its environment. Over time, the amount of carbon-14 decreases, so the rate at which the material produces beta particles from carbon-14 decay decreases, too. It is the beta particles, rather than the actual ratio of carbon-14 to carbon-12, that historically have been monitored to evaluate important archaeological objects. After about ten half-lives, it becomes difficult to detect sufficient beta particles to use carbon decay as a reliable dating strategy, so items that exceed sixty thousand years in age demand other dating techniques.

One estimate of the age of the Earth is determined by examining the ratio of uranium-238 to lead-206. Although the decay happens in a stepwise manner, the first step in the decay, with a half-life of  $4.5 \times 10^9$  years, is by far the slowest, and it controls the ratio. The age of rocks is dated using the following formula.



Here we assume that there was no lead-206 initially present, only U-238. This assumption seems valid because U-238 and Pb-206 are often found in the same rocks, while other isotopes of lead are not present. Let's assume we start with a mole, 238 grams of uranium. After one half-life, half the uranium would remain—119 g—and half a mole of lead-206, 103 g of lead, would have been formed. The ratio of the mass of Pb-206 to the mass of the U-238 would be  $103 \text{ g}/119 \text{ g} = 0.87$ . As time goes on, and more U-238 decays, the mass ratio will increase in a predictable way. So far, the highest Pb-U mass ratio found on Earth is 0.85. This ratio indicates that the rock was formed about one half-life ago. The half-life of U-238 is  $4.468 \times 10^9$  years. The age of the rock is estimated at 4.5 billion years. The Earth must be at least 4.5 billion years old.

Humans have always lived in an environment that includes natural radioactivity. Nuclear processes have been a part of science since radioactivity was discovered by Becquerel in 1896. Despite the terror of nuclear weapons, we have developed a number of helpful technologies since Marie Curie discovered two elements, radium and polonium, when she went searching for the components that make the minerals pitchblende and chalcocite more radioactive than uranium. Although many of us fear radiation exposure, it is important to note that nature is responsible for most of the radiation exposure we experience.

In addition to the dating strategies used above, radioactivity has found a helpful role in medicine.

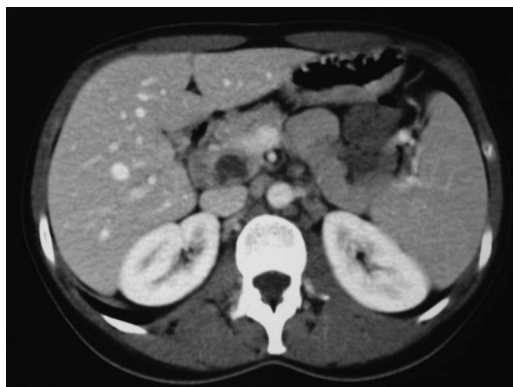
The isotope I-131 is used for thyroid treatment of Graves' disease. Iodine-131 undergoes beta decay with a half-life of about eight days. The beta particles it produces can penetrate several millimeters into living cells and are energetic enough to cause mutation and death in cells that it penetrates. In medical applications, appropriate high doses of the isotope are sometimes paradoxically less dangerous than low doses, since they tend to kill thyroid tissues that might otherwise become cancerous as a result of small mutations caused by exposure to low doses of radiation.

Although used in medical applications, I-131 is sometimes a major radioactive hazard. It was responsible for many adverse health effects because of atmospheric atomic bomb testing in the 1950s. A large quantity of I-131 was released in the Chernobyl disaster, and also in the nuclear crisis following the March 2011 earthquake and tsunami in Japan. This is because I-131 is biologically active and a major fission product from both uranium and plutonium decay, representing nearly 3 percent by mass of the total products of fission. Pharmaceutically, I-131 is produced from neutron irradiation of a natural tellurium target. This irradiation produces nearly 100 percent I-131 as the only radionuclide with a half-life



longer than hours.

Positron emission tomography (PET) is another medical procedure that depends on radioisotopes. The technique usually employs short-lived isotopes that include carbon-11 (~20 minutes), nitrogen-13 (~10 minutes), oxygen-15 (~2 minutes), and fluorine-18 (~110 minutes). These radionuclides are incorporated either into compounds normally used by the body, such as glucose (or glucose analogues), water, or ammonia, or into molecules that bind to receptors or other sites of drug action. Compounds specifically synthesized to incorporate radioisotopes are known as radiotracers. PET technology can be used to trace the biologic pathway of any compound in living humans (and many other species as well), provided it can be radiolabeled with a PET isotope. The medical and biological applications of PET are quite diverse. Radiotracers for new target molecules and processes are continuing to be synthesized; and dozens are in clinical use and hundreds are currently applied in research situations. Today, the most common radiotracer in clinical PET scanning is fludeoxyglucose, an analogue of glucose that substitutes some hydrogen atoms with fluorine-18.



A PET scan image showing the major organs of a human body. The scan was made using fludeoxyglucose as the main radiotracer component.

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The short half-lives of PET radioisotopes demand that they be produced using a cyclotron located nearby the PET imaging facility. The advantage of fluorine-18 is that its half-life is long enough that radiotracers labeled with it can still be useful even if they need to be manufactured off-site and shipped to imaging centers.

Brilliantly orange-colored Fiesta china produced in the United States between 1936 and 1944 can often be found for sale at antique shops and flea markets. The orange color is due to the uranium oxide in its glaze. It is still quite radioactive, although some experts contend that undergoing one x-ray examination causes greater radiation damage than using this china over a prolonged period. However, the Environmental Protection Agency warns consumers not to use radioactive-glazed ceramics routinely. Use with acidic foods may leach uranium, further increasing exposure. The manufacturer Homer Laughlin discontinued Fiesta red (their name for the orange pottery) in 1944.

Although nuclear processes are the source of all the elements in the universe, they are not the primary concern of chemistry. In our subsequent lessons, we will return to a focus on the chemistry important on our Earth. However, this detour into the origin of the universe has established some scientific principles that are of importance in the chemical as well as the nuclear world, so this interesting detour will provide the basis for some of our future discussions.

## For Greater Understanding

### Questions

1. One neutral atom of carbon-14 contains
  - a. 14 protons, 14 neutrons, and 14 electrons.
  - b. 6 protons, 8 neutrons, and 8 electrons.
  - c. 6 protons, 14 neutrons, and 6 electrons.
  - d. 6 protons, 8 neutrons, and 6 electrons.
2. An alpha particle is
  - a. a hydrogen-1 atom.
  - b. a hydrogen-1 ion.
  - c. a helium-4 atom.
  - d. a helium-4 ion.
3. Which of the following statements about the natural abundance of isotopes in the cosmos is true?
  - a. He is more abundant than H.
  - b. Co is more abundant than Fe.
  - c. Ni is more abundant than Cu.
  - d. Nitrogen is more abundant than carbon.

### Suggested Reading

American Chemical Society, and Jerry A. Bell. *Chemistry: A General Chemistry Project of the American Chemical Society*. New York: W.H. Freeman, 2005.

### Other Books of Interest

Hore-Lacy, Ian. *Nuclear Energy in the 21st Century: World Nuclear University Primer*. 2nd rev. ed. London: World Nuclear University Press, 2010.

Quinn, Susan. *Marie Curie: A Life*. New York: De Capo Press, 1996.

Rutherford, Ernest. *Radio-activity*. Vol. 1. Mineola, NY: Dover Phoenix Editions, 2004.

Soddy, Frederick. *The Interpretation of Radium*. Mineola, NY: Dover Phoenix Editions, 2004 (1912).

## Lecture 5

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### The Structure of Atoms

The Suggested Readings for this lecture are the American Chemical Society and Jerry A. Bell's *Chemistry: A General Chemistry Project of the American Chemical Society*, chapter 4: "Structure of Atoms," and Linus Pauling's *General Chemistry*.

The periodic table was developed through empirical methods. Dmitri Mendeleev (1834–1907) and Julius Lothar von Meyer (1830–1895) independently completed periodic tables in 1869, before the discovery of the proton, electron, or neutron. In this lesson we will discuss some of the analysis of the chemical and physical properties that allowed Mendeleev and Meyer to find order in the chaos of the chemical elements. We will then discuss the revolutionary world view developed beginning in 1895 and undergoing continuing refinements today—the quantum model of atoms. The quantum model allows chemists to develop a formal, mathematical theory of atomic structure that is accepted today because it explains the patterns so elegantly summarized in the periodic table.

In lecture 1, we discussed the density of materials, the ratio of mass to volume. Meyer considered the molar volume of the elements. The molar volume is determined by taking the inverse of the density and dividing by the molar mass.

$$V_{\text{molar}} = \frac{1}{d} \times M$$

Meyer's graph showed that Li, Na, K, Rb, and Cs had unusually high molar volumes. His graph of boiling points versus atomic mass showed that this same set of elements had relatively low boiling points, but that their neighbors F, Cl, Br, and I were even lower. Remember that the noble gases had not yet been discovered in 1869. Mendeleev focused on the chemical rather than the physical properties of the elements. He knew that Na, K, and Cs react violently with water and form one-to-one compounds with chlorine, bromine, and iodine. He left holes in his table where he thought elements that had not yet been discovered belonged. The subsequent isolation of these missing elements by other scientists was an early confirmation of the validity of the periodic table.

After the discovery of the electron, chemists were able to measure the ionization energies of the elements. The ionization energy is the amount of energy that must be provided to an atom to remove an electron from it, leaving a positive ion behind. The quantity is often measured by spectroscopic studies. In atoms with more than one electron, the first ionization energy is the amount of energy required to remove the outermost electron from the atom, leaving a +1 ion behind. The second ionization energy is the extra energy that must be provided to remove the second electron from the nucleus, leaving behind a +2 ion. The first twenty elements reveal a consistent pattern in their first ionization energies. He, Ne, and Ar have particularly high first-ionization energies; Li, Na, and K have particularly

low ionization energies. The other second- and third-row elements reproduce a zigzag pattern connecting the low ionization energies at Li and Na to the high ionization energies at Ne and Ar as we move across the periodic table. Spectroscopy provides another window into the organization of electrons in atoms.

Spectroscopy is the study of the interaction of light with matter. Although Newton perceived that solar radiation was continuous, technical advances allowed mid-nineteenth-century scientists to observe a series of dark bands, where no light appears, when solar radiation is dispersed appropriately. Robert Bunsen placed metal salts in his burner and observed the characteristic line spectra they emitted. The missing lines in the solar spectrum are the same as lines observed by Bunsen. Take sodium, for example. If you place sodium chloride in Bunsen's burner, you can clearly see the flame turn bright yellow. The yellow color is characteristic of the emission spectrum of sodium, and if you observe the light through a suitable grating or prism, you will see that it actually consists of two separate spectral lines, one with a wavelength of 589.0 nm and one at 589.6 nm. If, instead of loading Bunsen's burner with sodium chloride, you vaporize some solid sodium, and place it in the path of light emitted from a truly white light source, the sodium vapor absorbs these same two wavelengths of light, leaving dark bands in the otherwise continuous spectrum. The emission and absorption of light from elements is a reversible process. Today chemists and astronomers use visible spectra to identify the elements present in samples both in the lab and in remote locations. Chemists use highly refined devices called atomic absorption spectrometers and inductively coupled plasma spectrometers to quantitatively determine the amount of element in samples. The absorption and emission spectra identify an element just like a fingerprint identifies a person.

Before we examine how spectroscopy reveals the structure of atoms, let's remember some things about the nature of light. Light has a dual nature. At the very beginning of the nineteenth century Thomas Young (1773–1829) performed a series of experiments where he passed a collimated, single-color light beam through slits and observed the patterns the light produced on a screen beyond the barrier. It is easy for us to replicate Young's experiments today. Take a laser pointer and shine it on an index card or a business card. The card stops the light. If you have a very steady hand and a dark room, you can observe some of the pattern that Young first explained by blocking only half the beam with the card. If you don't have a steady hand, tape two cards to something that will hold them vertically. For example, place the laser pointer on a book on a table, pushed back from the edge, and shine it toward a flat wall. Tape the cards to two small boxes at a height that would allow the cards to stop the beam if you put the boxes on the table between the book and the wall. But place the cards on the table in positions where they don't block the beam, and you can see a clear laser pointer dot on the wall. Carefully slide the first card into the beam from one side until you block some of it. Then slide the other card in from the other side so that it would meet the first card, if you pushed them together. But don't push them all the way together. Leave the smallest possible space between the two cards. This is your slit.

Now look at the spot where the beam hit the wall. It will be easier to see if the room is as dark as possible. If your cards are close enough together—carefully push one toward the other if they are not—and in contrast to what you might expect, the light on the wall does not form a slit of light. Instead, you will see a series of alternating bright and dark bands on the wall. This pattern was familiar to Young and may be familiar to you as a diffraction pattern. Diffraction patterns are formed when waves overlap with one another. If you have ever dropped stones in a pond, you may have seen diffraction patterns form on the surface. Based on his observations, Young concluded that light travels through space like waves travel on the surface of water.

You can illustrate a wave by drawing an oscillating line on any surface. If you consider a piece of string as the material that makes a wave, the taut straight piece of string represents the null position of the wave. If you consider water waves made by dropping stones in a pond, the flat surface of the pond represents the null position of the water waves. When you wiggle the string or drop the stones, the material—the string or the water—is displaced from its null position. The height that the top of the wave reaches above the null position is called the amplitude of the wave. The valley of the wave is the same amplitude below the null position. The distance between the crests of two adjacent displacement maxima is called the wavelength of the wave. The velocity of the wave is the speed with which it moves through space. With water waves, you might measure the wavelength in units of cm, and the velocity in cm/sec.

If you keep your eye focused on one specific location in space and count the number of wave crests that pass that point in a second, you can determine the frequency of the wave measured in units of cycles/second. Lazy chemists usually just assign frequencies units of 1/second or  $\text{sec}^{-1}$ , also called “hertz” in honor of the radio pioneer Heinrich R. Hertz (1857–1894).

Scientists have agreed to represent the wavelength of the wave using the Greek letter lambda ( $\lambda$ ), the frequency using the Greek letter nu ( $\nu$ ), and the speed using a lower case  $u$ . A simple mathematical relationship is found to hold for these variables for many different types of waves. The equation is  $u = \lambda\nu$ .

If we apply this equation to a sound wave, rather than a water wave, we can calculate the frequency of sound. The speed of sound is 340 m/s (meters per second). A typical frequency of sound wave that humans can hear is  $1,700 \text{ sec}^{-1}$ . The wavelength of the sound wave at this frequency is then

$$\lambda = \frac{u}{\nu} = \frac{340 \text{ m/s}}{1,700/\text{s}} = 0.200 \text{ m} = 7.87 \text{ inches}$$

Sound and water waves are familiar to us. We know that each propagates through a different medium, sound waves through air and water waves through water. In the 1800s scientists asked themselves about the medium that propagates light waves. They knew

it was invisible and that it was present even in the vacuum of space, because sunlight propagated through space to the Earth. Although scientists made excellent progress in understanding the wave nature of light through the 1800s, it took almost to the end of the century to resolve the issue of the medium through which light propagated.

The resolution occurs in the United States. Albert Michelson (1852–1931), a professor of physics at the Case School of Applied Science, and Edward Morley (1838–1923), a professor of chemistry at the nearby Western Reserve University (now united as Case Western Reserve University), conducted experiments to detect the aether assumed to permeate the universe and carry light waves. By 1887, they improved their technology significantly and, using a precision interferometer, published results showing that the aether, if it existed, was moving at only a fraction of the speed one would predict based on the speed with which the Earth orbited the Sun. Although Michelson continued to refine experiments in this field, the results of the Michelson-Morley experiment are today taken as conclusive proof that there is no aether and that light, unlike sound or water waves, propagates without a medium.

James Clerk Maxwell (1831–1879) proposed the modern picture that light is composed of mutually perpendicular electromagnetic waves. Changing magnetic fields produce electric fields, and changing electric fields produce magnetic fields. These coupled, fluctuating fields make Maxwell's light self-propagating and independent of any medium. Furthermore, by the end of the 1800s it was well established that the color of visible light was correlated with the wavelength, and therefore the frequency, of the light. And it was determined that the invisible infrared and ultraviolet lights discussed in lecture 4 were also electromagnetic radiation, but with longer and shorter wavelengths, respectively, than the visible radiation that creates rainbows.

Today, technology gives us access to the entire range of the electromagnetic spectrum. Radio waves with wavelengths greater than 1 meter allow radio communications. Radar and cell phone signals propagate on waves down to about 10 mm in wavelength. Microwaves and infrared radiation cook our food, carry communication signals, and run electronic eyes. Visible light, with wavelengths from 750 nm in the deep red to 400 nm in the violet, allow us to see our world. Shorter wavelength radiation, from UV to x-rays, are used in medical applications and for materials testing. The highest energy, shortest wavelength radiation, gamma rays, allows us to probe the energetics of nuclei. Chemists use all of these types of electromagnetic radiation to investigate chemical behavior. But for now, let us return to the visible part of the spectrum.

If you have an electric stove at home, you know that the coils look red when they are hot—red hot. If you have ever seen a picture of a steel furnace, you know that molten steel glows white hot. If you know any astronomy, you know that astronomers give color names to stars—red giants, yellow dwarfs, or white dwarfs. Our sun is a yellow dwarf. These names are derived from behavior nineteenth-century physicists ascribed to objects called black-body radiators. A black-body radiator is an ideal system that completely absorbs and

emits all wavelengths of light. The hotter a black body, the more blue light it emits. The red coil of your electric stove emits lots of red light, but it does not emit much blue light. If we could increase its temperature, we could see its color shift as its temperature increased. It would become yellow, then green, then blue as the temperature increased, and the amount of radiation emitted at shorter wavelengths increased. Eventually, your stove would emit all colors of light to a significant degree, and we would perceive it as white hot. Of course stars are made of different stuff than your stove coil. But the principle is the same. Red stars are cooler than yellow stars, which are cooler than blue stars, which are cooler than white stars.

Throughout the nineteenth century, scientists believed that materials could store any amount of energy, and that materials interacted with light by absorbing and emitting a continuous distribution of energies. But there was one set of data that could not be explained using this assumption. The emission of hot black-body radiators in the ultraviolet did not behave the way it was supposed to. In working through the mathematics associated with the application of the wave theory of light, Max Planck realized that he could derive a mathematical description that would match the experimentally measured intensities of light from a black-body radiator if he assumed that the oscillating charges that emitted the electromagnetic radiation from the black body could have only discrete, rather than continuous, energies. In the language of mathematics, he had to sum the energies, not integrate them. Planck asserted that the charges in the black body could only have specific energies calculated by  $E = nh\nu$ , where  $n$  is an integer,  $h$  is a constant with units of energy\*seconds, and  $\nu$  is the frequency of the oscillator in the black body. If the black body wanted to absorb or emit energy, it could not absorb or emit any arbitrary amount of energy, but only specific amounts of energy,  $\Delta E$  where  $\Delta E = n_2 h\nu - n_1 h\nu$ .

In macroscopic terms, Planck's hypothesis can be interpreted as saying that if you climb on a swing, and begin to swing, you can swing at one swing per second, or two swings per second, or five swings per second. But you cannot get a push that causes you to swing at one and a half swings per second, nor at 4.36, nor at any other frequency except an integer number of swings per second. The rate at which your swing can move is quantized, not continuous. You must absorb or emit enough energy to move you from one to two swings per second, not the arbitrary amount someone may choose to push you with.

Planck chose a value of the proportionality constant  $h$  to best fit the experimental results from the black-body radiators he was trying to explain. Today the accepted value of  $h$ , called Planck's constant, is  $6.626 \times 10^{-34}$  J-s. In addition to limiting the frequencies of the oscillators in a black body, Planck's hypothesis illustrates another fundamental shift in the way scientists thought about light—the energy depends on the frequency of the light. Not on its amplitude. As you might expect, most scientists required independent confirmation before they could accept such exotic ideas.

In 1905, Albert Einstein (1879–1955) provided the confirmation, and more. The experiment that Einstein was trying to explain was the photoelectric effect. In the photoelectric effect, light hitting a metal surface knocks electrons off the surface. A battery

is connected between the metal surface and another conductive surface. Both surfaces are encased in an evacuated glass tube. When light strikes the metal surface it can cause electrons to be emitted from the surface. The electrons can fly through the evacuated glass tube and strike the second surface, which completes the circuit through a current meter. The voltage source is not so strong that it allows a current to flow. Using the traditional model of light as a wave whose energy is determined by its amplitude, scientists predicted that exposure to bright light should provide enough energy to knock electrons off the metal's surface and cause a current to flow. The data was not consistent with this model, however.

Experimentally, the color of the light was more important in causing the current to flow than the brightness. Essentially, when red light was used, no electrons were liberated, no matter how bright the light, nor how long the exposure. But if blue light was used, electrons were emitted, even at the lowest measurable intensities. Furthermore, the energy of the emitted electrons depended on the frequency of the light, not its intensity. Einstein applied conservation of energy to reason that the energy of the electron had to be the energy of the photon minus the energy required to remove the electron from the metal. He assumed Planck's model—that the energy of the light was proportional to a constant. When he analyzed the data, Einstein found that the proportionality constant from the photoelectric experiment was the same as the proportionality Planck had derived from the black-body problem. This demonstrated that light provided energy in discrete packets, that the energy of light was quantized, and that it is conveyed to material bodies in units of  $h\nu$ . Einstein called these packets photons.

The independent confirmation of Planck's proposal led scientists to accept it. But it did present them with a puzzle. The interference behavior of light can only be explained if it acts as a wave. But the photoelectric effect requires us to treat light as photons that deliver discrete amounts of energy, like particles, when they interact with matter. We say that light has a dual nature—it is both wave and particle. Today, the wave-particle duality of light is well accepted by scientists of all stripes and is exploited in both scientific studies and technological applications.

Once the quantized nature of the energy of light was established, it didn't take long for the idea to be applied to explain the spectra and structure of the atoms. Niels Bohr (1885–1962) is credited with making the fundamental intellectual breakthrough that has led to the modern era of quantum chemistry.

In the early 1900s, the structure of the atom presented scientists with a conundrum. The accepted model was that atoms were like a plum pudding, where the positive charge and the mass associated with it were spread fairly uniformly through space, while the electrons were buried in this positive sea like the plums in a classic British pudding. Some had proposed a nuclear model, with the heavy positive charges in the center and the lighter electrons around. But classical physics said that like charges repel and oppositely charged particles attracted each other, and that charges undergoing acceleration, such as those spiraling toward an opposite charge, should emit radiation. These principles argued against the nuclear model.



In 1909, Hans Geiger (1882–1945) and Ernest Marsden (1889–1970) started shooting alpha particles at gold foils. It took them a while to refine their experiment and to get the gold foils thin enough to demonstrate the structure of the gold atoms, but what their results ultimately demonstrated provides the foundation of modern chemistry. If the plum pudding model of atomic structure was correct, they expected to see the alpha particles travel directly through the uniform electrical environment of the gold foil with very little deflection.

For the most part, that was what they saw. But about one alpha particle in eight thousand was deflected by more than 90 degrees. Rutherford is famously quoted as saying it was “as if you fired a fifteen-inch (artillery) shell at a piece of tissue paper and it came back and hit you.” Nevertheless, Ernest Rutherford (1871–1937) derived equations to explain Geiger and Marsden’s results. He applied classical physics to determine the size, mass, and charge of the nucleus required to cause the alpha particle deflections observed by Geiger and Marsden. In his derivations, he assumed that the atomic number ( $Z$ ) represented the number of protons in the nucleus.

Bohr’s insight was to apply some classical physics to Rutherford’s nuclear model. Bohr worked out a model for any atom with one electron. He assumed that the nucleus was so heavy that it could be considered as a stationary center about which the electron traveled in circular orbits. He calculated the electron’s total energy as the sum of its kinetic energy of motion and its electrical potential energy in the field established by the positive charge on its nucleus. Then, because the atoms did not self-destruct and electrons did not collapse into nuclei, Bohr asserted that the force of attraction between the charged species had to be exactly balanced by the centrifugal force of the electron’s motion. Though today this seems trivial, it was a revolutionary assumption at the time. It defied the common understanding of the behavior of electrically charged bodies and implied that electrons in atoms behave as the planets about the sun. Nevertheless, Bohr asserted it because it matched the observation that atoms did not self-destruct. Then Bohr asserted one more thing—he asserted that the angular momentum of the electron had to be quantized in units proportional to Planck’s constant. The result of these assertions were that the velocity of the electron was quantized and that the allowed velocities could be calculated as integer multiples of the first, fundamental velocity. The integers (symbolized by the letter  $n$ ) are called the principal quantum number. The radius of the electron’s orbit could be calculated and was found to depend on  $n^2$ . As  $n$  increases, Bohr’s model predicts that the electron occupies a discrete state with a discrete total energy at a discrete radius from the nucleus.

When the electron moved from one stable orbit to another, the energy emitted (if it moved closer to the nucleus) or absorbed (if it moved further from the nucleus) could be calculated from Bohr’s model. This model agrees with the experimental observation that emission and absorption of light happen at the same frequencies. In hydrogen, the calculated results agreed with experimental observations to within 0.05 percent. The discrepancy can be explained by noting that the nucleus and the electron actually should

be treated as both moving about their mutual center of gravity. This correction brought the experiments and Bohr's model into uncanny agreement.

The era of the quantized atoms was born. Unfortunately, Bohr's model only works for atoms with one electron. Add a second electron, and the model completely breaks down. Nevertheless, Bohr's model is a useful picture of atomic structure and provides us with the terminology we continue to use today to describe the quantum structure of atoms and molecules. The stable orbit closest to the nucleus is called the ground state and labeled with principal quantum number  $n = 1$ . Its energy is negative, in keeping with the opposite charges between the nucleus and the electron and Coulomb's law. The energy of the allowed orbits is proportional to  $1/n^2$ . The energy of the second level is one-quarter as negative as the ground state, the third level one-ninth, and as the quantum number increases, the energy separation between the allowed quantum levels becomes smaller.

Bohr's model clearly gave a correct mathematical description of the behavior of the electron in the hydrogen atom, but physics had yet to resolve the philosophical question—how was it that electrons could occupy stable orbits around nuclei and not collapse into the nucleus? The reality contradicted everything classical physics knew from its study of macroscopic charged systems. In 1924, Louis de Broglie (1892–1987), in a remarkable summary of thirty years of revolutionary physics, postulated that if light could behave like both a wave and a particle, so could an electron. With absolutely no justification, except that the units worked, de Broglie asserted that the wavelength of an electron could be calculated by taking Planck's constant and dividing it by the electron's momentum, the product of the electron's mass times its velocity.

Soon after de Broglie made his hypothesis, two American physicists, Clinton Davisson (1881–1958) and Lester Germer (1896–1971), were able to use it to explain the results of their experiments. Davisson and Germer had used accelerated electrons rather than x-rays to investigate the structure of crystals. The x-ray data was well known and could be explained by assuming that the atom spacing in the crystal provided a variety of grating sizes that served to scatter the x-rays. Davisson and Germer found that when they accelerated electrons appropriately the interaction between the crystal and the electrons produced a diffraction pattern identical to that produced by the x-rays. Furthermore, the wavelength of the electron waves could be determined from the known spacing in the crystal lattice. Davisson and Germer's calculated wavelengths matched the de Broglie equation. Electrons were behaving like waves. Both light and waves had both particle and wavelike properties, depending on the experiment being conducted. Wave-particle duality was complete.

Subsequent refinements in the description of the electronic structure of the atoms depend on the application of wave mechanics. Werner Heisenberg's (1901–1976) uncertainty principle (1925) followed de Broglie's hypothesis by less than a year. The assertion that an electron can have wave-like properties allows us to explain the non-collapse of the electron into its nucleus in two ways. One, Bohr's hydrogen atom orbits

have circumferences that are equal to integer multiples of the wavelengths of the electrons that occupy them. In each allowed orbital, the circumference of the orbit is an integer multiple of the wavelength associated with an electron at that energy. The electron can therefore be considered a stable standing wave around the nucleus. Heisenberg's uncertainty principle, however, abrogates this simple standing-wave model. Heisenberg's principle says that you cannot know both the exact position and the exact momentum of an electron at the same time. There is an uncertainty in the position or the momentum that is inherent in the electron having wave properties. The magnitude of the product of the two uncertainties is, of course, directly proportional to Planck's constant. The inability to know both the position and the momentum simultaneously means that we cannot calculate a trajectory for the electron, like we can for the Earth around the sun, or for a bullet shot from a gun. The best we can do is calculate the probability of finding the electron in a small region of space, or the momentum in a small window of possible momentums.

Therefore, the description of the electron in the atom changes from being an orbit around the nucleus to a three-dimensional probability map of where the electron is likely to be in the space around the nucleus. Typical orbital pictures include the volume around the nucleus, where there is a 95 percent chance of finding the electron in that orbital. Even today, our pictures of the orbitals occupied by any electron are based on the simple probability maps derived for one-electron atoms.

What about atoms with more than one electron? We can gain a lot of insight into the structure of multielectron atoms by looking for patterns in their ionization energies. Hydrogen has one electron and one ionization energy—1,312 kJ per mole. It takes 1,312 kJ of energy to separate the electrons from a mole of ground-state hydrogen atoms, producing a mole of free electrons and a mole of  $\text{H}^+$  ions. Helium has two electrons and therefore two ionization energies. The lower ionization energy is required to pull the first electron away from each helium atom, forming one mole of free electrons and leaving one mole of  $\text{He}^{+1}$  ions behind. It takes 2,373 kJ/mol of energy to do that. Let's think simplistically about where the two electrons in helium can be and how that might cause the ionization energy of helium to be different from hydrogen.

Again, we assume that Coulomb's law governs the energy between the nucleus and its electrons. Remember that Coulomb's law says that the potential energy between two charged particles is given by the following equation:

$$\text{PE} = \frac{k Q_1 Q_2}{r}$$

Where  $Q_1$  is the charge on the nucleus,  $Q_2$  is the charge on the electron, and  $r$  is the distance between the electron and the nucleus. In every case when we consider a specific atom,  $Q_2$  and  $k$  are the same. The potential energy (PE) therefore depends on two things—it increases in magnitude when the nuclear charge increases, and it decreases when the radius between the nucleus and the electron increases. Now we have a simple model for

discussing electron organization in multielectron atoms. Let's compare hydrogen to helium. The nuclear charge in hydrogen is +1. The nuclear charge in helium is +2. It seems reasonable to assume that one of two things is true about the two electrons in helium. Either they are at the same radius from the nucleus or one is further from the nucleus than the other. If they are at the same radius, then the fact that the charge on the nucleus is double should mean that the ionization energy of helium should be about double the ionization energy of hydrogen. If the second electron is farther from the nucleus, the first electron will provide a shield, preventing the second electron from "seeing" the entire nuclear charge. In fact, even in the classical trajectory model of electrons, if the second electron is further from the nucleus than the first, the first inner electron should be moving fast enough that on average the second electron will see a net +1 charge at the center of its orbit—+2 from the nucleus and -1 from the electron. In this case, the ionization energy for the outer electron in helium should be less than the ionization energy of hydrogen, because the  $Q$  has stayed the same, but the  $r$  is bigger.

Which scenario is consistent with the data? The ionization energy required to take the outermost electron from helium is 2,373 kJ/mol. This is close to, but not exactly, twice the ionization energy of hydrogen, 1,312 kJ/mol. It is not less than the ionization energy of hydrogen. The ionization energy data indicates that the two electrons in helium are at the same radial distance from the nucleus. We know that the two electrons will repel each other and can use the electron-to-electron repulsion to account for the fact that the first ionization energy in helium is not quite double the ionization energy of hydrogen. The electron-to-electron repulsion makes it a little easier to remove the second electron. We say that the two electrons in helium occupy the principal quantum number 1 orbital.

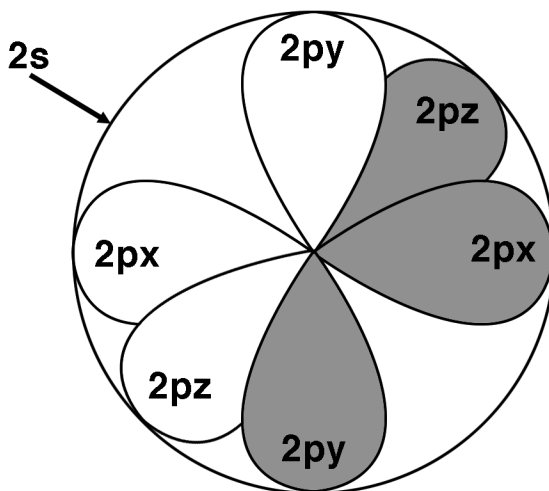
What about lithium? Now the nuclear charge is +3. Again we have two options. Either the third electron is at the same distance from the nucleus as the first two, or it is farther away. If it is at the same radius, we would expect the ionization energy to be about three times the ionization energy of hydrogen, because the nuclear charge is three times greater, but the radius is the same. Of course, now there are two electron repulsions to factor in, but we would still expect the first ionization energy to be larger in lithium than in helium if all three electrons are at the same radius from the nucleus. On the other hand, if the third electron is farther from the nucleus than the first two, the first ionization energy of lithium should be lower than that of hydrogen. As the third electron looks back at the nucleus it sees the +3 nuclear charge shielded by the presence of two inner electrons. It sees an effective charge of +1. With the same charge as hydrogen, but a larger radius, the ionization energy for that outer electron should be less than the ionization energy for hydrogen. What does the experiment say? The experiment shows that the first ionization energy for lithium is only 520 kJ/mol. This is a fraction of the ionization energy of hydrogen. The third electron clearly occupies a space at a larger radius from the nucleus than the first two electrons. We will call this principal quantum level 2.

We can continue the analysis of the first ionization energies to predict the relative radius

of each electron as we build up the number of electrons around the nuclei. If adding an extra electron causes the ionization energy to increase, then the new electron must be at about the same distance from the nucleus as the previous electron. If the ionization energy for the new electron goes down, then we know the new electron must be farther from the nucleus than the previous one. A clear pattern develops. Beryllium has a higher first ionization energy than lithium. The fourth electron is at the same radius from the nucleus as electron number 3. Boron's ionization energy is slightly less than the ionization energy of beryllium. Its extra electron is farther away from the nucleus, but not twice as far, like lithium was compared to helium.

If you continue this analysis as you move across the periodic table, the ionization energies generally increase until you get to sodium. The first ionization energy of sodium is again only about one-quarter the ionization energy of neon. It is even less than the first ionization energy of lithium. The eleventh electron is clearly farther from the nucleus than electrons number 3 through 10. After sodium, the first ionization energies increase again as you move to the right across the periodic table until you get to the nineteenth electron, in potassium. The nineteenth electron is clearly farther from the nucleus than electrons eleven through eighteen.

The analysis of the ionization energies within the context of Coulomb's law is sufficient to develop the gross structure of the atoms, without having to refer to the complicated mathematical formalisms of quantum mechanics. The positions of the electrons around the nucleus appear correlated with the periodic table. The electrons in hydrogen and helium are about the same distance from the nucleus. The third electron, the valence electron in lithium, is clearly farther away than the first two. Electrons four through ten all seem to be about the same distance from the nucleus, with minor variations that are so far unaccounted for. Electron eleven is clearly farther from the nucleus than four through ten, but the electrons through number eighteen appear to be at about the same distance from the nucleus as electron eleven. In quantum terminology, we call the regions of space occupied by the electrons "shells." It appears the shell closest to the nucleus can accommodate two electrons. The next largest shell, shell two, is at a larger average radius from the nucleus and can hold eight electrons, and the next shell, shell three, is still at a larger average radius and can also



A representation of the regions of space occupied by electrons in the 2s and 2p atomic orbitals. The nucleus is at the center of the sphere.

hold eight electrons. However, if we move to elements nineteen through twenty-seven, things become a bit fuzzier.

The wave equations developed early in the twentieth century resolve the questions of the structure of atoms in a more formal way. Erwin Schrödinger (1887–1961) set forth equations that replaced the equations of classical particle dynamics with equations whose solutions are given by mathematical functions that are called electron wave functions. In contrast to the algebraic calculation you might have seen in your high school or college physics course, Schrödinger's equation expands William R. Hamilton's (1805–1865) approach to classical mechanics, which applied Newton's calculus to solve physical problems.

The wave equations that satisfy Schrödinger's equation are identified with three different integers, which occur as parameters in the mathematical functions. The parameters cause the probability graphs of the wave functions to be different from one another, both in their shapes in three-dimensional space and in their average size.

The first quantum number is closely correlated with the most probable radial separation between the nucleus and the electron. It is called the principal quantum number,  $n$ . The second is called the angular momentum quantum number, labeled  $l$ . It gives the orbital angular momentum of the electron it describes. The third quantum number is called the azimuthal quantum number. It gives information about the relative orientations of the several orbitals that have the same orbital angular momentum. This quantum number is labeled  $m_l$ . Those of us who have had a course in differential equations will be familiar with the idea that the numbers that label the possible solutions to Schrödinger's equation are nested. The value of the first quantum number restricts the value of the second, which restricts the value of the third. The very abstract mathematics of the wave, or quantum mechanics, found rapid acceptance among scientists because its results correlated easily with the experimental results we have discussed here.

In complete agreement with the results of measurements of ionization energies, the formal math shows that in hydrogen, the lowest energy orbital, labeled  $1s$  to indicate that the principal quantum number is 1 and the angular momentum quantum number is zero, puts the highest probability of finding the electron closest to the nucleus—eerily close to Bohr's calculated radius for an electron orbit. The next higher energy, labeled with  $n = 2$ , but allowing the angular momentum quantum number to be both 0 and 1, indicates that the highest probability of finding the electron is farther from the nucleus than those described by  $n = 1$ . Furthermore, all the orbitals with  $n = 2$  have a node, a region of space where the wave function goes to zero, and the probability of finding the electron also goes to zero.

The wave functions can be pictured as standing waves in three-dimensional space around the nucleus. Like other standing waves, they have regions of positive deflection from the null position and regions of negative deflection from the null position. Between the positive and negative deflections are nodes, where the wave function has a value of zero. If the wave function has a value of zero at a certain point in space, the quantum mechanics says there is

no probability that the electron described by that function will appear in that location.

There is one further complication the ionization energies reveal. They suggest that both electrons in helium are at the same distance from the nucleus. This seems impossible, given that the electrons repel each other because they have like charges. A simple experiment illuminates a possible explanation. When a beam of helium gas is passed through a magnetic field, the atoms pass through the field without being deflected. When a beam of lithium atoms is passed through the same field, none of the atoms pass through undeflected. Instead, half the lithium atoms are deflected to the left and half to the right. Deflection is the behavior we expect if the atoms are themselves magnetic. Today, we explain the splitting of the beam of lithium atoms by invoking a property of electrons called *electron spin*. The electrons behave as if they are spinning about their own axis, as the Earth does about its axis. But unlike the Earth, electrons appear to be able to rotate in either direction—clockwise or counterclockwise.

Rotation in one direction produces a small magnetic field pointing one way. Rotating in the other direction produces a magnetic field pointing the opposite way. In helium, the two valence electrons appear to have opposite spins and therefore produce no net magnetic field in helium atoms. But the third valence electron in lithium does not have a partner to pair up with. Its spin means that a net magnetic field is associated with the atom. When a beam of lithium atoms passes through an external field, half of the atoms have magnetic fields aligned with the external field, and half have magnetic fields aligned opposite to the external field. The result is a split in the trajectory of the lithium atoms, half going left and half going right.

Although the mathematics describing quantum mechanics can be framed in either differential calculus or in matrix algebra terms, the results are always consistent and can be appreciated by an examination of the graphs of the functions in three-dimensional space, or by examining the energy distributions, which can also be extracted from the formal treatment. The orbitals in any atoms are identified by three quantum numbers. The principal quantum number  $n$  gives the average distance of the electron in the orbital from the nucleus. The angular momentum quantum number  $l$  can be interpreted as giving both the shape of the orbital in space and the angular momentum associated with an electron in that orbital. The magnetic or azimuthal quantum number  $m_l$  can be interpreted to give the orientation of the orbit around the nucleus or the projection of the angular momentum on an atomic or externally imposed field.

## For Greater Understanding

### Questions

1. The periodic table was developed
  - a. by the alchemists.
  - b. before the discovery of subatomic particles.
  - c. after the discovery of subatomic particles, but before the development of quantum mechanics.
  - d. after the development of quantum mechanics.
2. The potential energy of an electron relative to the nucleus in an atom is
  - a. positive because energy must be provided to hold the electron in the atom.
  - b. positive because of Coulomb's law.
  - c. negative because of Coulomb's law.
  - d. negative because energy is radiated as electrons orbit the nuclei.
3. The energy required to ionize one mole of sodium atoms is 496 kJ/mol. The energy associated with one mole of violet photons with a wavelength of 420 nm can be calculated from Planck's equation,  $E = h\nu$  (recall  $\lambda\nu = c$ ). Can one mole of violet photons ionize one mole of sodium atoms?

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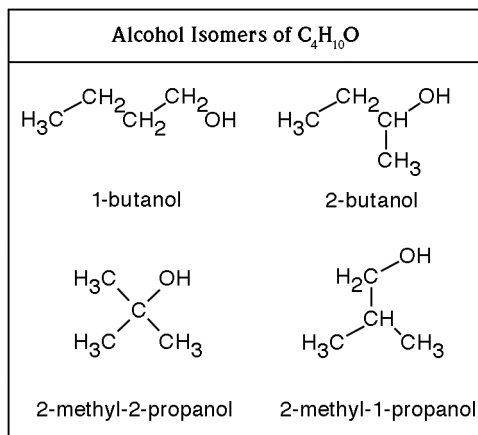
## Lecture 6

### The Structure of Molecules and Compounds

The Suggested Readings for this lecture are the American Chemical Society and Jerry A. Bell's *Chemistry: A General Chemistry Project of the American Chemical Society*, chapter 5: "Structure of Molecules," and Linus Pauling's *General Chemistry*.

In the last lecture, we examined the quantum description of the arrangement of electrons in atoms and confirmed that the presence of an octet of valence electrons seems to make atoms stable and resistant to chemical transformations. In lecture 1, we introduced the idea of Lewis diagrams as a convenient way to summarize the preference for octets shared by many elements on the periodic table. In this lecture, we will expand our discussion of Lewis structures, adapt the quantum model to describe molecular structure, and resolve some of the questions we have left open in the earlier lectures.

Remember from lecture 2 that structural isomers are chemical compounds that contain the same atoms, but the atoms are arranged in different ways in three-dimensional space. As the number of atoms in a covalent molecule increases, the number of possible isomers increases even faster. Let's consider the alcohol isomers of  $C_4H_{10}O$ . One isomer has the  $-OH$  on a terminal or end carbon. Another has the  $-OH$  on one of the middle carbons. The first compound,  $CH_3CH_2CH_2CHOH$ , is called 1-butanol. The second compound,  $CH_3CH_2CH(OH)CH_3$ , is called 2-butanol. These two are both considered straight chain alcohols, because the carbon backbone forms a straight line of carbon atoms. It is also possible to make two branched alcohols with this formula. In a branched compound, three of the carbons make a chain, but the fourth attaches to the central carbon, so the carbons form a "T" shape. If the three carbons attached to the middle carbon all have their valences filled by hydrogens, then the middle carbon fills its last valence by holding the  $-OH$  group. If one of the three terminal carbons has the  $-OH$  group, then the fourth valence on the central carbon is occupied by hydrogen. These are two different structural isomers. The compound with the  $-OH$  on the central carbon is called 2-methyl-2-propanol, or *tert*-butyl alcohol. The compound with the  $-OH$  on one of the terminal carbons is called 2-methyl-1-propanol, or *iso*-butyl alcohol. These compounds are similar in that they all have the same mass, the same number of valence electrons, and a  $-OH$  group. But their physical properties are dramatically different. *Tert*-butyl alcohol is miscible in water and has the highest



melting point and the lowest boiling point of the four. The 1-butanol is the least soluble in water, 9 g per 100 mL, and has an intermediate melting point but the highest boiling point of the four compounds.

This seems like a complicated series of properties to organize. All these alcohols have hydrogen bonding, because of the  $\text{-OH}$  groups. However, something else seems to be affecting their physical properties. If you think of the atoms in each molecule as if they are squishy spheres that glob together to make molecules, there are three general classes of compound structure that emerge: linear molecules, branched molecules, and spherical molecules. The shapes can determine the strength of the dispersion forces between them. All things being equal, you might expect the linear version of a molecule to have the highest boiling point because the extended structure allows lots of points of contact for the dispersion forces that hold the molecules together in the liquid. On the other hand, if you think about putting a bunch of balls in a container, the contact area between adjacent balls is much smaller than the contact area between adjacent logs. Therefore, the boiling point of the spherical molecules should be less than the boiling point of the linear form because the contact area between adjacent molecules is considerably less when molecules are spherically shaped, and not linear. The branched molecules should be somewhere in between. This reasoning is consistent with the reported boiling points of the  $\text{C}_4\text{H}_{10}\text{O}$  isomers. But the trends in melting points are a little harder to explain on the basis of molecular geometry, because they depend on the specific way the molecules pack into the solid structure.

Now we want to move forward by applying the quantum theory to describe the structure and energetics of molecules. We have already stated that molecules are communistic in how they distribute their valence electrons in a covalent molecule—all the valence electrons get thrown in the pot and distributed as needed to minimize the energy of the entire collection of nuclei and electrons. We have already established that quantum mechanics places electrons in atoms in specific parts of space we called orbitals. A molecule is inherently a more complicated environment, with multiple nuclei attracting the electrons and more electrons repelling each other. Just as we used the simplest atom, hydrogen, as the basis for the quantum description of atoms, we will use the simplest molecule, the molecular ion  $\text{H}_2^{+1}$ , as the basis for the quantum description of molecules.

The  $\text{H}_2^{+}$  molecule is a three-body problem. The potential energy term in the Schrödinger equation for the molecule contains three terms: an attractive, negative contribution to the total energy from the potential energy between the electron and each of the two hydrogen nuclei, and a repulsive, positive potential energy contribution because the two nuclei repel each other. Finally, because we are treating the nuclei as fixed, there is one positive contribution to the total energy because of the kinetic energy of the electron.

To solve the Schrödinger equation for the molecule, we must fix the distance between the nuclei. The fixed distance between the nuclei is called the bond length. The repulsion between the like nuclear charges means that the two nuclei have a minimum potential

energy when they are infinitely far apart and the potential energy is zero. The presence of an electron is therefore essential in permitting the formation of a molecule. The potential energy between the electron and either nucleus is always negative, because of the opposite charges. Since there are two attractive components of the potential energy and only one repulsive component, the net potential energy becomes more and more attractive as we bring the three particles closer and closer together. But we also know that as the electron is confined to a smaller volume of space, its kinetic energy increases. You can see a physical analogy of this behavior in coin funnels at the mall—the plastic cones that you launch a quarter in, and at first it rolls slowly, but then it rolls faster and faster as the diameter of the cone narrows, until it is flying around almost horizontally before it drops out the bottom of the cone. In a molecule, as the three particles come closer and closer together, the net potential energy becomes more and more negative. At the same time, the kinetic energy becomes more and more positive. Fortunately for us, the rate at which the potential energy becomes more negative is not the same as the rate at which the kinetic energy increases. The total energy of the three-body system is high and positive at very small internuclear distances where the combination of nuclear repulsion and kinetic energy dominates. But as the nuclei move apart, the total energy eventually becomes negative, allowing a stable  $\text{H}_2^+$  molecule to form. The bond length is given by the intermolecular distance, which yields a minimum in the total energy curve. As the nuclei are pulled yet farther and farther apart, the total energy becomes less and less negative as the repulsive contribution to the potential and the kinetic energy of the electron become smaller.

It is not possible to exactly solve the Schrödinger equation for the  $\text{H}_2^+$  ion, so we must approximate the solutions. One straightforward way to approximate the molecular orbitals is to treat them as combinations of the atomic orbitals for the one electron atom. In  $\text{H}_2^{+1}$ , the first molecular orbital is taken to be a combination of the two 1s orbitals on the two hydrogen atoms. Conceptually, we simply allow the two 1s orbitals to overlap in space. The electron is then shared between the nuclei, and the probability of finding the electron is cylindrically symmetric around the bond axis, the imaginary line that connects the two nuclei. The arrangement of the two nuclei and the electron has a lower total energy than the separated hydrogen atom and  $\text{H}^+$  nucleus. Sharing the electron between the two nuclei both contributes the extra attractive term to the potential and minimizes the kinetic energy by allowing the electron to occupy an extended volume in space. Therefore, the  $\text{H}_2^{+1}$  molecular ion is stable. In atoms, we named the spherically symmetric orbitals s orbitals. To clearly distinguish molecular orbitals from atomic orbitals, we name the cylindrically symmetric molecular orbitals sigma orbitals and use the lower-case Greek letter  $\sigma$  to label them.

In the case of a sigma bond formed between two different nuclei, the cylindrical symmetry is maintained, but the electron density is enhanced near the more electronegative of the two nuclei.

Every single bond in a molecule's Lewis dot diagram represents a sigma bonding orbital. Each sigma orbital accommodates two electrons with opposite spins. When an atom has several valence electrons and participates in multiple bonds, like carbon in methane, the 2s and three 2p orbitals morph into a set of four  $sp^3$  hybrid orbitals, which allows the formation of four equivalent sigma bonds, occupying mutually exclusive regions of space around the central atom. Lone pairs of electrons in molecules occupy orbitals that are commonly called nonbonding sigma orbitals, labeled  $\sigma_n$ .

In covalent compounds formed of second-row elements, the total number of bonding and nonbonding sigma orbitals always adds up to four orbitals per second-row nucleus. The four hybrid orbitals resemble fattened exclamation-point-shaped volumes around the atom. In a molecule of  $F_2$ , there are eight sigma orbitals. In  $CH_4$ , there are four, H being a first-row element. In  $CF_4$ , there are twenty. You will recall that we defined the shape of molecules by the relative geometries of the nuclei that compose them. Orbitals identify the regions of space occupied by the electrons. Therefore, it is not always the case that the electron geometry and the molecular geometry are the same. In particular, if nonbonding sigma orbitals contain electrons, the molecular geometry will be different from the orbital geometry, although in every case the orbital geometry determines the molecular geometry by locating the bonding electrons in space.

The second four sigma orbitals in the second-row elements C and N overlap with the 1s orbitals of the hydrogens to form  $CH_4$  and  $NH_4^+$ . The four sigma orbitals point toward the corners of a tetrahedron. A very convenient model showing the shape of the sigma bonding orbitals in tetrahedral molecules is a set of four standard balloons. When inflated, balloons are wide at the top but grow narrow as they approach the tie off. If the four tie offs are joined together, the region where they overlap identifies the position of the central C or N atom in these molecules. The bond angles in any tetrahedral molecule match calculations from the Schrödinger equation, locating the minimum energies of the nuclei relative to one another at an H-C-H or H-N-H angle of 109.5 degrees.

In ammonia and water, the number of bonding sigma orbitals is three and two, respectively. The balance of the sigma orbitals are nonbonding. Because a nonbonding orbital interacts only with one nucleus, the energy associated with the electrons occupying it is not lowered as much as the energy associated with a bonding orbital. Also, the nonbonding orbitals maintain more of their s character. They are wider and more rounded than the elongated sigma bonding orbital. Because the orbitals must occupy mutually exclusive regions of space, the larger size of the nonbonding orbitals constricts the angles between the sigma bonding orbitals in ammonia and water. As a result, the H-N-H bond angle in ammonia is 107 degrees and the H-O-H angle in water is 104.5 degrees.

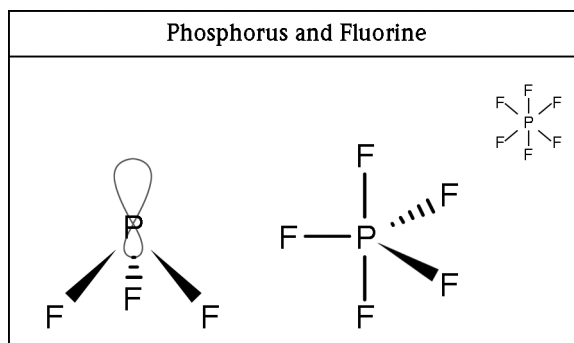
Calculations show that the increasing nuclear charge from C to N to O causes the sigma bonding orbitals to move closer to the nuclei, so that the C-H bond length, 109 pm, is larger than the N-H bond length, 101 pm, which is larger than the O-H bond length, 94 pm. In general, as in atoms, the orbital radii decrease when the nuclear charge increases.

Because hydrogen, oxygen, carbon, and nitrogen are abundant elements in living things, the geometry of compounds containing these second-row elements is of particular interest to organic chemists and biochemists. However, some third-row elements also play important roles in biochemistry—especially phosphorus, sulfur, and chlorine. How is bonding to these elements like that of the second-row elements, and how is it different? Remember that we generally separate the core electrons in an atom from its valence electrons. One substantial difference between second- and third-row atoms is the size of its core electron cloud. The core of the second-row elements contains only the 1s electrons. The one s orbital is quite small compared to the 2s and 2p orbitals. And the 2s and 2p orbitals are smaller than the 3s and 3p orbitals. Therefore, it seems possible that the larger size of the third-row core might allow third-row elements to accommodate more than four sigma orbitals.

There are two known neutral compounds of phosphorus (P) and fluorine (F),  $\text{PF}_3$  and  $\text{PF}_5$ . Spectroscopic data shows that all three P-F bonds in  $\text{PF}_3$  are equivalent and that the molecule is polar. The same data shows that  $\text{PF}_5$  has two similar but slightly different P-F bonds, but the molecule is nonpolar. Since P is a third-row element, the second-row rule no longer applies. The twenty-six valence electrons in  $\text{PF}_3$  cannot be distributed in twelve sigma bonding and nonbonding orbitals. However,  $\text{PF}_5$ , which has forty valence electrons, should be able to accommodate its valence electrons in the twenty sigma bonding and nonbonding orbitals the second-row rule predicts. Let's draw Lewis dot diagrams for these species, keeping all this information in mind.

The  $\text{PF}_3$  molecule has a Lewis diagram that is identical to that for ammonia. This is not a surprise, as P is directly below N on the periodic table and F is directly below H. The P is in the center, connected via a single bond to each F. Each F's valences are filled by three nonbonding electron pairs. This accounts for twenty-four of the twenty-six valence electrons, meaning that a final nonbonding lone pair is available to complete the valence on the central P atom. The orbital geometry around each atom in the molecule (including the F's) is approximately tetrahedral, but as we noted before, the nonbonding lone pairs of electrons take up more space than bonding electron pairs, so the bonding pairs around the central P are likely compressed to slightly smaller bond angles than a perfect tetrahedral. The fluorines are surrounded by three large clouds of nonbonding electrons providing the  $\text{PF}_3$  molecule with a virtual halo of negative charge. For this reason, even though the structure of  $\text{PF}_3$  is quite similar to the structure of  $\text{NH}_3$ , their chemistries are quite different.

When we consider the  $\text{PF}_5$  molecule, we have to take advantage of the larger core on the P atom. The data on  $\text{PF}_5$  indicates that all five fluorines must be connected via a sigma



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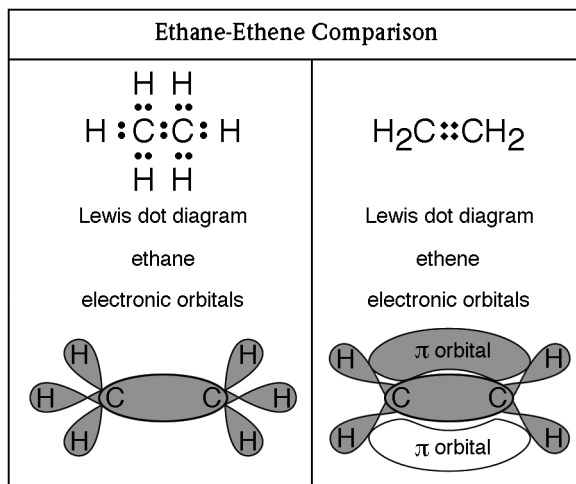
bonding orbital to the central P. This requires the P atoms to be able to accommodate five sigma bonds. Both experiment and calculation indicate that it does this, the first of several violations of the octet rule we will see in third-row elements. Because the molecule contains five fluorines, it must have twenty bonding and nonbonding sigma bonds. The molecular structure demands five bonding sigma orbitals, and satisfying the valences of the fluorines takes the remaining fifteen in nonbonding sigma orbitals. The five bonding orbitals form by morphing together the 3s, three 3p, and 3d orbital. The resulting  $sp^3d$  hybrid orbitals are arranged in a trigonal bipyramidal structure around the central P and stretch between the P and each of the F's in turn. Three of the fluorines point toward the corners of an equilateral triangle in a plane containing the P. The other two fluorines are on a line perpendicular to the plane through the P, one above and one below the plane of the three fluorines. There are two different bond angles in the molecule. The F-P-F angle in the plane is 120 degrees, while the F-P-F angle between a fluorine in the triangle, the phosphorus, and a fluorine above the plane is 90 degrees. These two bond angles produce two slightly different environments for the fluorines in the plane and the fluorines on the line, confirming the behavior observed spectroscopically.

Let's examine a molecule in which the atoms attached to the central atom are different from the H or F atoms in  $CH_4$  or  $CF_4$ . An interesting case is when all four substituents are different, for example,  $CHClBrI$ . The H, Cl, Br, and I are attached to the central carbon with sigma bonds and form a tetrahedral structure. You can draw a bunch of different Lewis diagrams for  $CHClBrI$ . Of course, those drawings are two-dimensional representations of a three-dimensional object, so we know the order in which we draw the Lewis diagram doesn't matter, right? Right. However, in your mind's eye, when you convert the molecules to a three-dimensional structure, things can be different. Arrange the models so that you are looking down the H-C bond. Rotate the molecule so the Cl is pointing toward twelve o'clock. There are now two possibilities—either the Br is at four o'clock and the I is at eight o'clock. Or vice versa. Whichever one you have, no matter how you try to reorient it, you cannot superimpose the two models by reversing the positions of the Br and the I. The structure with the Br at four o'clock is not the same as the structure with the I at four o'clock. In fact, the two forms are mirror images. They are called stereoisomers. When pure samples of these two stereoisomers interact with polarized light, they rotate the light in opposite directions. These two are optical isomers of each other.

So far, all the molecules we have discussed in this lecture are centro-symmetric molecules—they have an atom in the center to which all the other atoms are bonded. But centro-symmetric molecules, while of great interest in presenting the basic principles of chemical bonding and structure, represent only a small fraction of the known molecules. So now we will expand our discussion to include a variety of other types of molecules.

In lecture 2, we discussed the difference between saturated and unsaturated fats. In general, a saturated molecule is one in which all the valences of the carbon atoms in the molecule are satisfied by the presence of a bonding sigma orbital occupied by a shared

electron pair. In contrast, in unsaturated molecules, there is one or more carbon-carbon multiple bonds. The simplest unsaturated hydrocarbon, ethene,  $\text{C}_2\text{H}_4$ , can be contrasted to its saturated cousin, ethane,  $\text{C}_2\text{H}_6$ . The Lewis diagram for ethane shows that each carbon is bound to three hydrogens, with its fourth valence satisfied by sharing an electron pair through a sigma bond with the carbon. The geometry about each carbon is tetrahedral. Both the H-C-H and the C-C-H bond angles are  $109.5^\circ$ . We haven't mentioned this before, but the  $\text{CH}_3$ 's are free to rotate their positions relative to each other about the C-C single bond, just like Tinkertoys can be rotated about on the sticks that connect them.



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What about  $\text{C}_2\text{H}_4$ ? The Lewis dot diagram shows that two hydrogens are attached to each C by a single bond. This uses up all the atoms in the molecule but leaves an extra valence electron on each carbon. Both carbons are surrounded by seven, not eight, electrons. The Lewis rules say that the remaining valence electrons get combined together to form a second bond between the two carbons. We say that the carbons are connected by a double bond. Experiments show that double bonds are shorter and more stable than single bonds.

Of course, we know that four electrons cannot share the same part of space. The double bond in ethene forms from the overlap of p atomic orbitals on the two carbons. The electron density is located above and below a plane containing the two carbon atoms and the sigma bond between them. The double bond consists of a sigma bond and a pi bond. The pi designation indicates that the orbital contains a node in a plane containing the two nuclei, just as p atomic orbitals have a node at the atomic nucleus. Despite the node, which makes it appear there are two parts of space occupied by the electrons, the orbital represents one region in space occupied by the pair of electrons that form the bond. Remember that the electrons are being treated as waves, and a single wave can have many nodes, but we still recognize it as a single entity. Electron orbitals are the same.

The Lewis dot diagram of  $\text{CO}_2$  requires two double bonds—one between the C and each of the oxygens. The two pi orbitals are perpendicular to each other, if the O-C-O nuclei are in the plane defined by a paper, one pi orbital has its two lobes above and below the paper, the other in front of and behind the paper. The pi orbitals are mutually perpendicular, one spanning each C-O sigma bond.

A more complicated picture is required for the carbonate ion,  $\text{CO}_3^{2-}$ . The Lewis dot diagram requires a double bond to allow all four atoms to satisfy the octet rule. However,

spectroscopic observations show that all three C-O bonds are equivalent. The Lewis diagram formalism addresses this issue by requiring three resonance forms, each showing a double bond between one O and the carbon. We understood that the true picture was given by morphing all three of these together, but we don't have a good way of doing that in the Lewis formalism. In the LCAO-MO approach, the C in carbonate has three different sigma bonds, one pointing toward each of the oxygens. But its low energy pi symmetry orbital can be formed by overlapping the p orbitals from all the atoms. This orbital contains the pi electrons and makes all three CO bonds equivalent in bond length and bond strength.

The rigidity of pi bonds means that isomers can exist when pi-bonds are present. There are, for example, two forms of 2-butene, a four-carbon chain where there is a double bond between carbons 2 and 3. One has the two methyl groups on the same side of the molecule, called "cis," and one has the methyl groups on opposite sides of the double bond—"trans." The two compounds have the same molecular mass, and both are nonpolar. But they have different boiling points, trans = 1°C, cis 3.7°C. The cis-trans conversion of retinal, a molecule, is essential for vision. The isomeric structure of biomolecules definitely affects the function of the molecules.

The discussion so far has focused on a formalism called linear combination of atomic orbitals-molecular orbitals, LCAO-MO. It is very amenable to pictorial interpretation, and the pictures it produces are consistent with the physical properties of lots of chemicals. More sophisticated versions of molecular orbital theory are used when the LCAO-MO picture falls short.

So far, we have focused on molecular bonding and structure. But not all chemicals are molecules. Consider two quite different kinds of solids—ionic and metallic. In ionic solids, individual ions are held together in specific geometries by Coulombic forces. This is often a very strong type of bonding, making solids that have high melting points, are brittle and hard to cut, but conduct electricity when melted or dissolved in a solvent. Often the three-dimensional structure of an ionic solid is reflected in the shape of its crystals. If you look at the sodium chloride crystals in your salt shaker under a magnifying glass, you will see tiny cubes reflecting the cubic arrangement of the ions on an atomic level.

Metals are quite different in properties from ionic solids. They can be pounded into foils, pulled into wires, and are relatively easy to cut. Some have quite low melting points when compared to ionic solids. As solids, they conduct heat and electricity. These properties are observed because the valence electrons in a solid metal occupy orbitals that spread over all the atoms in the metal sample. Chemists often describe the metallic bond as a "sea of electrons" surrounding the positive atomic cores. Essentially, metal orbitals are shared by all the atoms in the metal. The delocalized nature of their electrons accounts for metal's malleability, ductility, lustrous appearance, high conductivity, and high heat conductivity.



## For Greater Understanding

### Questions

1. Draw Lewis structures for the following compounds and identify the number of sigma and pi bonds in each.
  - a. Ozone,  $\text{O}_3$
  - b. Hydrogen cyanide,  $\text{HCN}$
  - c. Ethanol,  $\text{CH}_2\text{CHOH}$
2. Which of the following statements is true?
  - a. The electrical conductivity of sodium is higher than the electrical conductivity of copper.
  - b. The electrical conductivity of nitrogen gas is higher than the electrical conductivity of copper.
  - c. The electrical conductivity of copper is higher than the electrical conductivity of nickel.
  - d. The electrical conductivity of solid sodium chloride is greater than the conductivity of solid copper.

### Suggested Reading

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## Lecture 7

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### Chemical Reactions

The Suggested Readings for this lecture are the American Chemical Society and Jerry A. Bell's *Chemistry: A General Chemistry Project of the American Chemical Society*, chapter 6: "Chemical Reactions," and Linus Pauling's *General Chemistry*.

So far, we have focused on the structure and properties of atoms and molecules. Of course, the real value in chemistry lies in chemical reactions. In this lecture, we will introduce the major classes of chemical reactions and discuss some of their consequences for making new materials and for converting or storing the energy that drives modern civilization. As in all our discussions of things chemical, the attraction between negatively and positively charged entities underlies all of the reactions we will discuss.

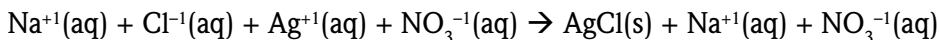
With some chemical combinations, it is easy to see that a chemical reaction is occurring. If you put some baking soda in a cup half full of vinegar, a dramatic mass of bubbles appears immediately. If you drop an iron nail in a puddle of rainwater, it does not take long for red flaky rust to appear.

Perhaps the simplest example of opposite charge attraction causing a reaction is the precipitation of ionic salts. Sodium chloride, the most familiar ionic salt, is soluble in water. In fact, virtually all salts containing a +1 cation and a -1 anion are soluble in water. We'll note the exceptions in a moment.

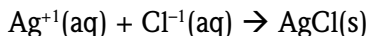
In 1887, one of the earliest notable female chemists, Ellen Swallow Richards, used the fact that silver and chloride form an insoluble precipitate of  $\text{AgCl}$  to map out the concentration of  $\text{Cl}^-$  in the waters of the state of Massachusetts. Salt was ubiquitous in human activity, used as a food preservative and in a variety of industrial applications. Richards tested more than forty thousand water samples from across the state and established the first map of polluted waters.

Richards's tests can be replicated in a chemistry lab. A solution of sodium chloride dissolved in water can be mixed with a solution of silver (I) nitrate dissolved in water. The two solutions look exactly like pure water, which is one reason chemists are neurotic about labeling every bottle in every lab. When the salt and the silver nitrate solutions are mixed together, a change is immediately obvious. The solution turns milky, and after a few minutes a solid, the silver (I) chloride precipitate, begins to settle to the bottom of the container. The solid can be separated from the solution by filtration and weighed, as long as the chloride is the limiting reagent. In other words, the chloride gets used up in the reaction, but some silver ion is left over. The mass of the silver chloride precipitated tells you the mass of chloride ion in the original solution.

The following is the reaction describing this precipitation:



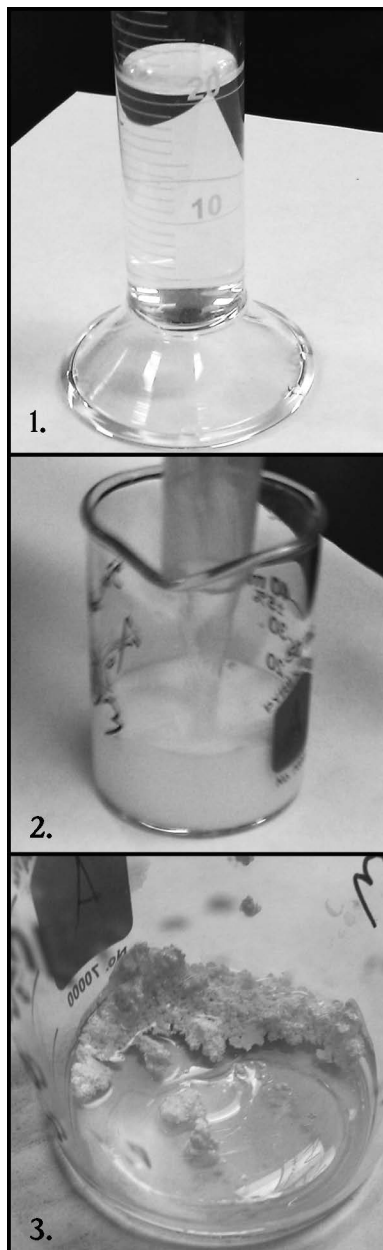
The sodium and nitrate are called “spectator ions” because they do not participate in the reaction but are present in the solution. Chemists often omit the spectator ions and focus on the net precipitation reaction.



This reaction is balanced—it has the same number of each type of ion on the reagent and product sides of the arrow, and the total charge is zero on each side. The equation tells us that silver and chloride react with a 1:1 stoichiometry—one silver ion combines with one chlorine ion to make one AgCl formula unit, or one mole of silver ions combines with one mole of chloride ions to make one mole of silver chloride. Ellen Richards kept very careful records of the concentration of the silver nitrate solutions she made, the volumes of those solutions used in the precipitation reactions, and the masses of AgCl formed as a result of her tests. The stoichiometry of the silver-chloride precipitation allowed her to deduce the mass of the chloride that was in her water samples.

We do not observe precipitation reactions very often in our everyday lives. But we are familiar with the consequences of several precipitation reactions. Stalagmites and stalactites form when calcium carbonate precipitates from dripping groundwater in caves. Kidney stones are precipitates of calcium phosphate and calcium oxalate that can cause excruciating pain as they pass through the body.

The second category of reaction we will consider is the acid-base reaction. Historically, there have been three major definitions of acids and bases. The earliest definition focused on the ions formed by the disproportionation of water. Acids are compounds that produce  $\text{H}^+$  in aqueous solutions. Bases are compounds that produce  $\text{OH}^-$  in aqueous solutions. Aqueous solutions, those with a pH equal to 7, are considered neutral. Those with a pH less than 7 are considered acids, and those with a pH greater

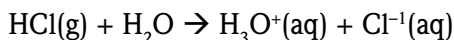


Images showing Professor Sauder’s replication of Ellen Swallow Richards’s 1887 lab experiment to map out the concentration of sodium in water.

than 7 are considered bases. It is worth taking a moment to discuss the pH scale. The pH scale is a logarithmic scale, like the Richter scale, that describes earthquakes, or the decibel scale that describes the intensity of sound. Logarithmic scales are used to describe phenomena that cover a huge range of magnitudes. Most simply, the log of a number tells its relative order of magnitude. In the decimal system, the log of 1 ( $\log 1$ ) = 0; the log of 10 = 1; the log of 100 =  $\log 10^2$  = 2. The log of 1,000 =  $\log 10^3$  = 3, and so on. An increase of 1 in the log scale means that the absolute number has increased by 10. An earthquake that rates a 5 on the Richter scale is ten times stronger than an earthquake of magnitude 4. The pH scale has the extra complication in that it includes a negative sign. This simply inverts the order of things. A solution with a pH of 4 has ten times the concentration of hydrogen ions as a solution with a pH of 5. For every unit increase in the pH, the concentration of hydrogen ions in the solution decreases by a factor of ten.

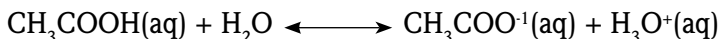
A later definition of acids and bases focuses on the reactions that occur between acidic and basic molecules. According to the Brønsted-Lowry theory (named for Johannes Brønsted and Thomas Lowry in 1923), an acid is a proton donor in a reaction, and a base is a proton acceptor. Remember that an  $H^{+1}$  ion consists of a proton only, because it has lost its electron in forming the +1 ion.

Today, the Lewis definition (named for G.N. Lewis) is the most comprehensive definition of acid-base behavior. Lewis's focus on the behavior of electron pairs carries over to his definition of acids and bases. In a chemical reaction, the Lewis acid accepts a pair of electrons. A Lewis base donates a pair of electrons. Being able to draw correct Lewis dot diagrams for the compounds participating in acid-base reactions is essential to being able to identify the Lewis acid and base. The first type of Lewis acid-base reaction results in the transfer of a hydrogen ion from one compound to another. It is closely related to the Brønsted-Lowry definition of acid-base reactions. Consider the reaction that occurs when hydrochloric acid gas is dissolved in water.



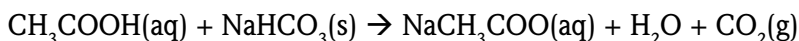
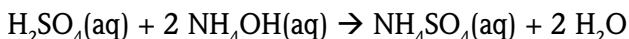
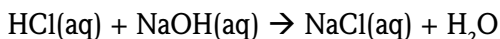
If you draw the Lewis dot diagrams for HCl and  $H_2O$  it is easy to see that in this reaction the hydrogen +1 ion from the HCl is transferred to the  $H_2O$ , forming  $H_3O^+$  hydronium ion and leaving a  $Cl^{-1}$  ion behind. The  $H^+$  acts as an electron pair acceptor and the water as an electron pair donor. The HCl is considered an acid in this reaction, and the  $H_2O$  a base. HCl is a strong acid—essentially, all the HCl's present donate their hydrogen ions to water molecules when HCl dissolves in water. That's why the reaction is shown with a one-way arrow. The HCl solution is highly conductive and has a pH determined by the HCl concentration.

In contrast, acetic acid, the active ingredient in vinegar, is a weak acid. When  $CH_3COOH$  is dissolved in water, some of the H's originally attached to the oxygen atoms are transferred to water molecules.



The acetic acid molecule is considered the acid, as its hydrogen accepts a pair of electrons from the water molecule, forming an acetate anion and a hydronium cation. Note that there is a double-headed arrow in this equation. This arrow means that only a small fraction of the acetic acid molecules are actually dissociated in vinegar solutions. In the reverse reaction, treating  $\text{CH}_3\text{COO}^-$  and  $\text{H}_3\text{O}^+$  as the reagents, the  $\text{H}_3\text{O}^+$  acts as an acid. Its hydrogen accepts an electron pair from the O in  $\text{CH}_3\text{COO}^-$ , so the  $\text{H}_3\text{O}^+$  is called the conjugate acid in this reaction, and the  $\text{CH}_3\text{COO}^-$  is called the conjugate base. The extent of dissociation when a weak acid dissolves in water depends on the relative strengths of the base and the conjugate base in the reaction. When the strength of water is compared to acetate anion, the acetate anion is the substantially stronger base. The acetate anion forms a strong covalent bond with the H ion and is the majority component in the solution. The pH of this solution is less than that of pure water, but it is higher than the pH of an equivalent concentration of HCl.

When an acid combines with a base, the generic description is that they form a salt and water. The following are some examples of acid-base reactions that occur in solutions:



This last reaction is the reaction between vinegar and baking soda, showing that the production of  $\text{CO}_2$  gas accompanies the neutralization.

The second category of Lewis acid-base reactions involves metal ions that form complex ions with molecules and ions that can donate electrons to the metal. The complexes form when metals have d orbitals available to take electron pairs. Many metal-ion complexes are colored and are familiar to us from the names of pigments used by artists—cadmium yellow, cobalt blue, chromium oxide green. However, different ligands can cause metal complexes to have different colors. The color changes reflect the extent to which the metal-ligand complex reorganizes the electronic energy levels associated with the metal in contrast to the energy levels of the isolated metal ion and ligand species. Because of the relatively large size of the d orbitals, complexes can sometimes accommodate six ligands in an octahedral arrangement around the central metal atom. For example, an aqueous solution of nickel (II) chloride is green. The nickel forms a complex with six water molecules, the oxygens from each water molecule donating one pair of electrons each to minimize the total energy of the system. If you add drops of concentrated ammonia solution to an aqueous solution of  $\text{NiCl}_2$ , the color changes from green to blue as the stronger base ammonia displaces the water molecules. The product formed is a complex ion with the formula  $\text{Ni}(\text{NH}_3)_6^{+2}$ . The stronger base dimethyl glyoxime can then be added dropwise to the nickel ammonia complex to form a bright red complex,  $\text{Ni}(\text{dmg})$ , which precipitates from the solution, releasing two  $\text{H}^+(\text{aq})$  ions. Before the advent of spectroscopic methods, the appearance of the red  $\text{Ni}(\text{dmg})$  was the definitive test for nickel in solutions.

The study of metal complexes belongs to the branch of chemistry called inorganic chemistry. The structure of metal complexes continues to be an area of active investigation because complex metals have wide applicability. Both chlorophyll (magnesium) and heme (the oxygen-carrying component of hemoglobin-iron) get their colors and their biological functionality from the energetics and chemistry of the complex environment.

In all of these examples, the metal ion acts as a Lewis acid, and the ligands as Lewis bases. It is appropriate in this introductory course to consider that the ligands are donating electron pairs to unoccupied orbitals in the metal atom or ion.

The application of the Lewis model extends into all areas of chemistry, not just general and inorganic. In fact, the reactions that populate the dreaded organic course, bane of premeds, are best understood in terms of electron pairs looking for the lowest possible energy configurations. In organic chemistry, a different set of terms is used to explain the behavior of the electron pairs. Electron-rich areas, which we have so far identified as Lewis bases, are called nucleophiles, meaning nucleus loving. Electron-deficient areas, which have an effective positive charge, are called electrophiles, meaning electron loving. Organic chemists often draw Lewis dot diagrams of reagents in chemical reactions and use arrows to indicate how electrons from nucleophilic regions in one molecule move to electrophilic regions in another molecule, causing a chemical reaction. The movement of electron pairs often causes a major rearrangement between the first products formed (called intermediates) and the final, chemically stable products of these reactions.

The second half of the twentieth century has been called the age of polymers by many scientists. The word “polymer” was coined to describe the structure of a variety of both naturally occurring materials (rubber, cellulose, and protein) and synthetic materials (for example, polyesters and nylon). Polyesters are formed when two types of monomers—a diacid and a dialcohol—react. In order to form the long chain required to call the product a polymer, both ends of the monomer molecules must be reactive. In the chemical synthesis of polyesters, the nucleophilic part of the alcohol (near the oxygen atom), is attracted to the electrophilic component of the acid—the carbon atom of the  $\text{-COOH}$  functional group. Following a rearrangement process, the intermediate in this reaction produces a water molecule and leaves behind an ester. The alcohol and acid are connected together by an oxygen atom bridge. Because water is produced in this reaction, it is called a dehydration. If both the acid and alcohol are di-functional, their other ends can participate in identical reactions, producing more waters and stringing more monomeric beads on the polymer chain. Nature has produced a myriad of polymeric materials.

There is a third class of reactions that can be described by electron transfers. The very dramatic reaction that occurs when sodium metal is thrown in water is a great example. In that reaction, solid metallic sodium is converted into sodium ions, water is ripped apart and forms hydrogen gas, and there is enough heat generated to catch the hydrogen on fire, despite the presence of water.

A more prosaic example is the conversion of iron to rust. A generic description of the iron-to-rust reaction is  $4 \text{Fe(s)} + 3 \text{O}_2\text{(g)} \rightarrow 2 \text{Fe}_2\text{O}_3\text{(s)}$ . In reality, rust is generally a hydrated form of iron oxide, and the presence of water makes the reaction more complicated than this equation indicates. A more useful example is the conversion of coal to carbon dioxide,  $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$ . These are all examples of oxidation. In the case of iron and sodium, oxidized means that the original element combines with oxygen to form a compound. Taking  $\text{Fe}_2\text{O}_3$  as the formula for rust, we would categorize rust as an ionic compound in which the metal, iron, has a charge of +3, and the nonmetal oxygen, has its charge of -2. This makes the overall formula neutral. But an interesting thing has happened to the iron. It starts out as a reagent in the reaction as neutral iron metal and has converted to  $\text{Fe}^{+3}$  ions. Somehow, each iron atom has lost three of its electrons. A more general definition for oxidation is then that an atom loses or gives away electrons in a chemical reaction. Of course, in chemical reactions, electrons do not just disappear; they are transferred to another element. When rust forms, the electrons are transferred from the iron to the oxygen atoms. Oxygen starts out as neutral atoms in a covalent molecule but becomes two negatively charged ions when it accepts the electrons from the iron atoms. The oxygen atoms are said to be reduced. Whenever there is an oxidation process occurring, there is a reduction process right alongside. The transfer of electrons from one element to another is called an oxidation-reduction or redox reaction.

When elements combine to form ionic compounds, it is easy to identify the species undergoing oxidation and the species undergoing reduction. The element that ends up with a positive charge is oxidized; the element that ends up with a negative charge is reduced. But when the products are covalent, it is harder to envision the electron transfer. Let's look at the formation of carbon dioxide from carbon and oxygen gas.

In their elemental states, carbon as graphite and oxygen as a diatomic gas are both neutral. Each atom on the reagent side is considered to have an oxidation state of zero. The oxidation state of any element is zero. The oxidation state of a monatomic ion equals its charge. But we need a method for determining the oxidation state of elements in covalent compounds.

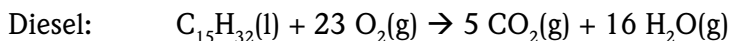
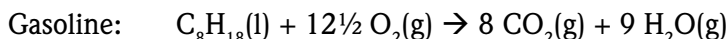
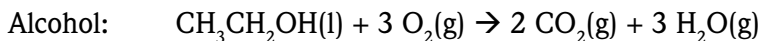
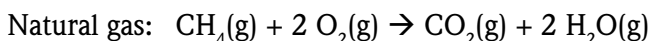
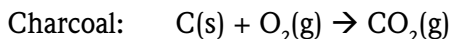
The calculus is different here than in assigning formal charge. The oxidation state reflects the charge that atoms in molecules have when all the shared electrons are assigned to the more electronegative partner. In the example in which carbon plus oxygen makes  $\text{CO}_2$ , recall that the Lewis diagram for  $\text{CO}_2$  puts the C in the center, with both oxygens double bonded to the carbon and both having two lone pairs. In assigning oxidation state, we give the four electrons from the double bonds to the O atoms. That gives them eight electrons, compared to the six each O brings to the molecule. So each of the oxygens in carbon dioxide has an oxidation state of -2. The carbon atom ends up holding no electrons, which means that it has an oxidation state of +4. The molecule remains neutral, and the sum of the oxidation states equals zero.

If we write the reaction for the oxidation of carbon— $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$ —and interpret it from the perspective of changes in oxidation state, the carbon goes from oxidation state 0 (zero) in its elemental form to oxidation state +4 in the compound. Each carbon atom in the reaction gives away four electrons and is oxidized. Each oxygen accepts two of the electrons from the carbon, reducing its oxidation state to  $-2$ . Both oxygens are reduced by accepting two electrons from the carbon atoms.

Redox reactions that start with elements and produce a binary product are trivial to balance. Unfortunately, many redox processes take place in aqueous environments and have complicated stoichiometry. But it is easy to understand these processes if you break them in half and consider the oxidation process independently of the reduction process. In the end, the two halves of the process need to transfer the same number of electrons—this is the key to balancing a redox reaction using the method of half-reactions.

Because oxidation-reduction reactions produce and consume electrons, a clever arrangement of the two halves of the reaction can form a battery, pushing electrons through an external conductor and forming a current that can do work.

The discussion of the oxidation states in carbon dioxide above allows us to identify combustion as a type of oxidation-reduction reaction. The complete combustion of carbon-containing compounds combines the carbon containing fuel with oxygen, available from the atmosphere, and produces carbon dioxide gas and water as the products. Anyone who understands the fundamentals of how gasoline is used to move a car is familiar with combustion. The nominally balanced reactions for the combustion of many fuels can be written by inspection—that is, looking at the reaction and adding the oxygen needed.





## For Greater Understanding

### Questions

1. When a compound containing carbon and hydrogen is burned in air, what products are always made?
  - a. Carbon dioxide and oxygen
  - b. Carbon dioxide and water
  - c. Water and hydrogen
  - d. Carbon and water
2. Precipitation reactions produce
  - a. a soluble ionic compound.
  - b. an insoluble ionic compound.
  - c. a soluble molecular compound.
  - d. an insoluble molecular compound.
3. In oxidation-reduction reactions
  - a. electrons are transferred from the species that is oxidized to the species that is reduced.
  - b. oxygen combines with an element.
  - c. electrons are transferred from the species that is reduced to the species that is oxidized.
  - d. oxygen is released as a product.

### Suggested Reading

American Chemical Society, and Jerry A. Bell. *Chemistry: A General Chemistry Project of the American Chemical Society*. New York: W.H. Freeman, 2005.

Pauling, Linus. *General Chemistry*. New York: Dover Publications, 1988 (1970).

### Other Books of Interest

Kean, Sam. *The Disappearing Spoon: And Other True Tales of Madness, Love, and the History of the World from the Periodic Table of the Elements*. New York: Little, Brown & Company, 2010.

Wolny, Philip. *Chemical Reactions* (Science Made Simple). New York: Rosen Central, 2011.

## Lecture 8

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### Chemical Energetics

The Suggested Readings for this lecture are the American Chemical Society and Jerry A. Bell's *Chemistry: A General Chemistry Project of the American Chemical Society*, chapter 7: "Chemical Energetics: Enthalpy," and Linus Pauling's *General Chemistry*.

In this era of the energy crisis, it is obvious that modern life is absolutely dependent on a variety of energy sources. Historically, the modern energy era began with the development of the steam engine in the early 1700s. The branch of chemistry concerned with energy transformations has its roots as a science in studies of this era. Today, it is called thermodynamics.

Take a moment and think about the variety of fuels you use or benefit from every day. When your alarm clock goes off, it is most likely powered by electricity from the grid, or by batteries. If you drive to work, you likely benefit from the combustion of gasoline or diesel fuel. You probably heat your home using natural gas, or electricity, and are less likely, according to census statistics, to use fuel oil, LP (liquid petroleum), gas, or wood. In 2011, in the United States, more than half of the electricity was generated by the combustion of coal, and natural gas was the fastest growing source of electricity. You might find a natural-gas-powered vehicle in your community, but they are just beginning to be available to consumers. Most of our transportation is powered by combustion of gasoline, diesel, and alcohol. So what is combustion? Why does our modern society prefer to burn coal to generate electricity, but gasoline to power cars? The answer to the first question is one we will answer here. The latter question is less about the chemistry than the politics—but I hope that clarifying the chemistry of combustion will help you understand some of the scientific arguments that are raised when the political aspects of energy production and consumption are discussed.

When you burn wood to heat your home, or gasoline to run your car, fuel is consumed and chemical energy is converted to heat and released from the chemical system to its surroundings. In the case of the woodstove, we want to maximize the amount of heat produced by the combustion. In the case of your car, the heat is a side product. We would like to minimize it to maximize the amount of work that can be done by your engine to move your car down the road. Let's formalize the chemical definitions of these terms.

Chemical energy, heat, and work are all forms of energy. The first law of thermodynamics says that energy is conserved in chemical transformations. The first law was established by British physicist James Joule, who undertook a systematic study to optimize the efficiency of steam engines in the early 1800s. In the combustions we will consider, the fuel is a carbon-containing compound. When combined with oxygen, the fuel is oxidized, yielding chemical products (ideally carbon dioxide and water) and heat.

Chemists understand that heat, or thermal energy, is a measure of the kinetic energy of molecules as they move through space. The kinetic energy of a molecule depends on its mass and its velocity squared:  $KE = \frac{1}{2} mv^2$ . Of course, we don't talk about the heat of air or its average molecular velocity; we report the temperature of air. Temperature is directly related to both the average kinetic energy of the molecules in a sample and the distribution of those kinetic energies. When a hot sample of air is compared to a cold sample of air, the hot air molecules are moving at a higher average velocity. The hot air also has a higher percentage of its molecules moving at high kinetic energies. Because of this, the motion of hot molecules appears more chaotic than the motion of cooler gas molecules. A good analogy for the high-velocity, random motion that characterizes a hot gas may be the balls used in lottery drawings. Initially, all the balls are sitting at the bottom of a large container. But then a high-velocity air jet is turned on and pushes the balls into rapid random motion. If you watch a slow-motion version of lottery balls being mixed, you would see an example of a relatively cold gas sample. At regular speed, the lottery balls provide an example of a hot gas sample. This chaotic motion may help keep you warm in the winter, but it won't help move your car down the road or provide electricity to recharge your cell phone.

In order to move your car or recharge your battery, we need to harness the heat produced in combustion and organize it to do work. Work is defined as a force applied to move a mass through a distance. Using the combustion of gasoline to move your car doesn't change the chemistry of the combustion at all, but a good engineer manages the combustion to control the way the chemical products and the heat produced interact with their environment to turn this chaotic kinetic energy into work. This work is sufficient to move your one-ton automobile down the road or to turn generators to make electricity to light up all the cities in the world every night of the year.

How is kinetic energy converted to work? Let's do a thought experiment. Imagine you have a very tall, very skinny pot and you put a cup of water in the bottom of it. It is tall enough that no water would splash out the top even if you brought the water to a full boil. Now imagine that you have a really wide balloon that can take the place of the lid of the pot. After you place the water in the pot, you add the balloon in place of a lid. Further imagine that the heat from the stove only heats up the water; it doesn't affect the balloon directly at all. When you turn the stove on and heat the water, what happens?

You should recall from our introduction that liquid water does not expand very much when it is heated. Certainly not enough to affect the balloon at the top of the very tall pot. But eventually the water will get hot enough to boil. When 1 mL of water boils it is converted to steam that occupies a volume of more than 1.2 L. It expands to twelve hundred times its original volume. Even in a very tall pot, it will not take long for the steam to begin to push on the lid. In this case, because the lid is a balloon, it will expand as more and more water is converted to steam. Is it obvious to you that the expanding balloon is doing work? What if we replace the balloon by a piston. As more and more water converts to steam, the piston will be raised higher and higher in its chamber. Lifting a weight against

gravity is a classic definition of work. In both the balloon example and the piston example, we have harnessed the random motion of gas molecules to cause the directed motion of a mass—the balloon or the piston—through space. Both of these are examples of work being done by a chemical transformation.

How do we measure heat, energy, and work? All are different manifestations of the same thing—molecular motion—and all are measured in the same units. The most familiar unit might be the calorie, with a lower case “c.” This calorie (c) is formally defined as the amount of heat required to change the temperature of 1 g of water from 14.5°C to 15.5°C at a constant pressure of 101.325 kPa (1 atm). Nominally, we use 1 cal/g-deg as the heat capacity of liquid water at any temperature. To make things just a bit confusing, we use the symbol  $c_p$  for heat capacity. The “P” subscript reminds us that the calorie is defined for transitions at constant pressure.

The food labels you read regularly record the heat or energy content of your foods in units of upper case “C” calories. A nutritional calorie (C) is equal to 1,000 c calories. In this course you can see why I prefer to use the metric unit of energy or heat—the joule. One c calorie is equal to 4.184 J. For the rest of this lecture, we will use joules as the unit of heat, work, and energy.

How can we measure the heat associated with a chemical process? Most measurements are made by applying what is commonly called the zeroeth law of thermodynamics. The zeroeth law says that when two bodies at different temperatures are put in contact with each other, heat flows from the hot body to the cold body until their temperatures are equal. So, for instance, if you place 100 mL of cold water, say 10°C, in a room-temperature room, say at 25°C, we know that heat will flow into the water until it is also at 25°C. In this case, the room is so large that the heat it loses to the cold water is negligible compared to the heat content of the entire room, and it is difficult for us to measure any temperature change in the room. However, since we know that it takes 1 cal or 4.184 J to raise the temperature of 1 g of water by 1°C, and we know that water has a density of 1 g/mL, we can calculate the amount of heat that has been supplied to the water:

$$\text{Heat} = q = \text{mass of water} \times \text{heat capacity} \times \text{temperature change} = m \times C_p \times \Delta T$$

$$q = (100 \text{ mL} \times 1 \text{ g/1 mL}) \times 4.184 \text{ J/g} \cdot ^\circ\text{C} \times (25^\circ\text{C} - 0^\circ\text{C}) = 6,276 \text{ J of heat transferred}$$

A typical heat capacity for air is about 1.012 J/g-°C. The density of air is 1.3 kg/m<sup>3</sup>. Assume a typical room is about 3 m × 4 m × 3 m tall = 36 m<sup>3</sup>. It holds 1.3 kg/m<sup>3</sup> × 36 m<sup>3</sup> = 46.8 kg = 46,800 g of air.

The temperature change associated with transferring the 6,276 J of heat from the air to the water is as follows.

$$-6,276 \text{ J} = 46,800 \text{ g} \times 1.012 \text{ J/g} \cdot ^\circ\text{C} \times \Delta T \text{ so } \Delta T =$$

$$-6,276 \text{ J}/46,800 \text{ g} \times 1.012 \text{ J/g} \cdot ^\circ\text{C} = -0.13^\circ\text{C}$$

Note a few things—first, heat flows into the cold water. In this sample, I have chosen to identify the cold water as the “system.” When heat flows into a system it is considered to be a positive amount of heat. The room is then considered the surroundings. The heat that flows into the system has flowed from the surroundings. The heat change in the surroundings is equal in magnitude, but opposite in sign, to the heat change in the system. Therefore, the heat flow from the surroundings is considered to be a negative quantity. In every thermodynamic analysis, the first thing to do is to clearly identify the system and the surroundings.

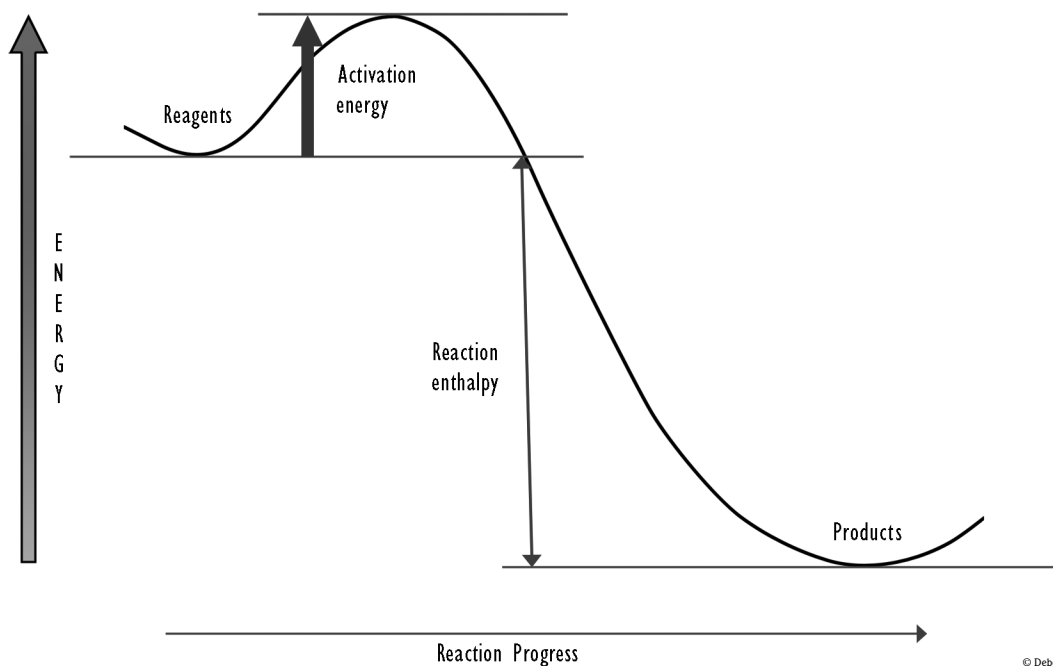
In our example, we have implicitly assumed that both the system and the surroundings are “closed.” That means that the system cannot exchange matter with its surroundings or with any other part of the universe. In introductory chemistry classes, the focus is generally on closed systems. Open systems are important in biology—all living systems are open systems—and in some geology and environmental applications. But for our purposes, the mathematical complications associated with open systems do not illustrate the fundamentals of thermodynamics, so all the systems we discuss will be closed systems. Also, in introductory chemistry courses, we assume that the system and surroundings together form an “isolated” system. An isolated system is one that cannot exchange matter or heat with the rest of the universe. When we ignored the temperature change of the “room” in the example we just discussed, it was because any room where we actually did this experiment would be exchanging air and heat with the space outside it. In order to actually detect the 0.13 degree temperature reduction in the room, the room would have to be completely sealed and perfectly insulated. Neither the typical house nor the typical laboratory is going to allow you to detect this temperature change.

In lecture 7, we discussed that much of chemistry consists of atoms trying to find ways to minimize their total energy—kinetic plus potential. When we consider combustion as a source of work, heat, or energy, we see that the reaction allows its chemical components to move from a relatively high total energy to a lower total energy situation. To see what happens when the transformation occurs, we just need to zoom out a bit and consider a bigger picture of things. Let’s start with the combustion of coal in oxygen. The chemical reaction is pretty simple:  $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + \text{energy}$ .

From an atomic perspective, this reaction requires us to pull carbon atoms apart and to pull the two oxygen atoms apart and jam the carbon atom in the middle between the two oxygen atoms to form carbon dioxide. We know this transformation produces energy in the form of both heat and light, so we know that the products must have less chemical energy than the reagents to allow energy to be conserved in the combustion process. Chemists draw diagrams showing how the chemical potential energy changes over the course of the reaction. We start with  $\text{C(s)}$  and  $\text{O}_2\text{(g)}$  as the reagents, and we see that we need to put energy into the system initially to pull the carbons apart and to pull the oxygens apart. The energy we put in is called the activation energy for the reaction. Once the reaction starts, the  $\text{CO}_2$  product molecules have much lower chemical energy than the carbon and oxygen

we started with. The potential energy diagram looks like a cross cut through two mountain valleys (see Figure 8.1). The reagents are in a high valley. When the reaction begins, the reagents move up the mountain, converting to intermediates. The activation energy is the energy required to move the reagents from the high valley to the top of the mountain. From the top of the mountain, it is all downhill to the much lower valley, where the products are. The overall energy released by the reaction is represented by the difference between the lowest point in the high valley and the lowest point in the low valley. This is the net energy released in the reaction. A sketch of this picture, showing a flat region in the high valley, the mountain, and the low valley, can be drawn for any combustion reaction. If it is drawn to scale, it is called a potential energy diagram.

Figure 8.1: Energy Changes Over the Course of the Reaction



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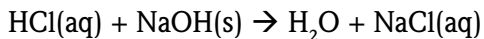
What about the work part? Work means moving a mass against an opposing force. When you burn coal, does this happen? I guess the answer is that it depends. If we build a super-strong container and seal all the coal and oxygen in it and burn the coal, heat is generated, but as long as the container doesn't break, no work is done, because nothing moved against an opposing force during the combustion. This super-strong closed container means that the reaction happened at constant volume. The heat associated with this experiment is equal to the energy change in the reaction.

If we conduct the reaction in a container with a piston in place of its lid, the situation would be different. As the reaction proceeded, oxygen gas would be consumed, but hot carbon dioxide gas would be produced. The hot carbon dioxide gas molecules have a higher kinetic energy than the cooler oxygen gas molecules did. They collide with the piston more forcefully than the oxygen gas did. The hot carbon dioxide therefore pushes the piston up in the cylinder. This does work, in the amount  $w = -P_{\text{ext}}\Delta V$ . The numerical quantity associated with the work is negative. We say that the system does work on its surroundings.

Whenever the pressure of the gas inside the piston is greater than the pressure outside the piston, the piston moves. Obviously, the larger the volume change associated with the combustion, the more work it can do. When the reaction occurs in a piston container, we consider this reaction to be occurring at constant pressure, not constant volume. Heat is still produced, but this time work is done, too. The amount of heat produced at constant pressure is different from the amount of heat released when the reaction was conducted at constant volume. We call this amount of heat at constant pressure the enthalpy of the reaction. The enthalpy change is given the symbol  $\Delta H$  (assuming we begin and end both the constant volume and the constant pressure transformations at the same temperature conditions,  $\Delta H = \Delta E + P\Delta V$ ). Remember that these variables all need to be considered from the point of view of the system. In our specific example, the energy of the system has gone down during the chemical transformation. When work is done by the system on its surroundings,  $\Delta V$  is greater than zero, so the work is negative. In our example  $\Delta E$  and  $\Delta H$  are both negative. Since the work is negative,  $\Delta H$  is less negative than  $\Delta E$ .

Using this definition of pressure-volume work, reactions that generate or consume gas produce the largest differences between  $\Delta E$  and  $\Delta H$ . Reactions that occur in solution, like precipitation reactions, are subtle. There is no obvious volume change, but if we use an open container, like a beaker on a lab bench, it's the pressure, not the volume, that stays constant. A subtle complication in many thermodynamic experiments is that conducting the same reaction from the same initial conditions of temperature, pressure, and volume does not necessarily imply that the products will end up at the same final conditions. In fact, the heat associated with a transformation at constant volume is different from the heat associated with the same transformation conducted under constant pressure conditions, so the products end up at different temperatures, and therefore at different final states. In thermodynamics, it is important to include the energy change required to make the final states equivalent—or you are comparing apples to oranges. But this subtlety is too often ignored in general chemistry courses.

The practical approach to determining the heat associated with chemical transformations is called calorimetry. In addition to combustion calorimetry, one common experiment is solution calorimetry. Let's take 200 mL of 0.5 M hydrochloric acid solution in a container and measure its temperature with a thermometer. If we add 4.0 g of solid sodium hydroxide, NaOH, to the mixture, the sodium hydroxide dissolves and reacts with the HCl. The reaction is as follows:



As the reaction proceeds, the temperature increases. Energy is released in this reaction. The products are at lower energy than the reagents. We say that the reaction is exothermic, but we want numbers. How exothermic is it? If we want to get reliable results from our experiment, we should define the system as the HCl and NaOH, and the surroundings as the water in the container. With this definition, we are recognizing that all the heat released by the reaction is absorbed by the water, increasing the temperature of the solution. We get the best measurements if we set up our reaction so that all the heat stays in the solution and does not escape into the rest of the universe. One way to do this is to conduct the reaction in a Styrofoam cup. We know that Styrofoam cups reduce the rate at which heat is lost from hot liquids. Styrofoam cups are usually good enough for a general chemistry course. More accurate measurements are made in the equivalent of a very high-quality thermos bottle, which includes a well-insulated lid. In very detailed work, the heat capacity of the calorimeter, and not just the water, becomes important and is determined independently of the experimental measurements being conducted.

Let's consider that we have a coffee cup calorimeter, with a lid. The lid has a hole in the top so that a thermometer can be placed in contact with a solution in the calorimeter. We pour 200 mL of 0.5 M HCl solution into the calorimeter and close the lid. We record the temperature of the solution using our thermometer. After a few minutes, we open the lid and quickly add the NaOH pellets. We replace the lid, gently swirl the cup to mix the reagents, and again begin reading the thermometer. What happens?

The neutralization reaction  $\text{HCl(aq)} + \text{NaOH(s)} \rightarrow \text{H}_2\text{O} + \text{NaCl(aq)}$  occurs quickly. The temperature of the solution increases. The exothermic reaction is releasing heat. After a few minutes, the temperature of the solution stabilizes at a temperature higher than the initial temperature. Can we determine the heat generated by the reaction?

Recall that the definition of a calorie is that it is the amount of heat required to raise the temp of 1 g of water by 1°C. If we assume that the thermal behavior of aqueous NaOH, HCl, and NaCl is not too different from the behavior of water, we have enough information to determine the heat produced. We have 200 mL of solution and added 4.0 g of NaOH. Assume the solution's density is pretty much unchanged in the reaction and is 1 g/mL. If it's not, the math just gets messier, but the principle is the same. Then the heat generated by the reaction is as follows:

$$q = (1 \text{ cal/g } ^\circ\text{C}) \times (200 + 4.0) \text{ g} \times (T_{\text{final}} - T_{\text{initial}})$$

If the temperature increases from 25 to 36.75°C, the heat associated with the reaction is 2,398 cal. Since we used 200 mL of 0.50 M HCl and 4.0 g of NaOH, we have produced 2,398 cal of heat and 0.10 mol of NaCl. Therefore, the heat of the reaction is -23,982 cal/mol or -23.98 kcal/mol.

Let's do another experiment. This time start with 0.10 moles of solid NaOH and 200 mL of distilled water. If we again measure the temperature of our water, and then add the solid



NaOH and watch the temperature as it dissolves, we see that this is also an exothermic process. The heat we measure is called the heat of solution of NaOH. The heat of solution of NaOH is  $-10.63 \text{ kcal/mol}$ .

Let's repeat the experiment one more time, but this time use 100 mL of 1.0 M HCl(aq) and 100 mL of 1.0 M NaOH(aq). When these two solutions mix together, the temperature again goes up. We can calculate the heat  $q$  produced by the neutralization in the same way that we did when we used the solid NaOH reagent. Notice that at the end of the experiment we again have 200 mL of 0.50 M NaCl. We have again produced 0.10 moles of NaCl. But the amount of heat produced in this experiment is different from the amount of heat produced when we added the solid NaOH to the HCl solution. That makes sense, because the reagents are different. The first reaction was  $\text{HCl(aq)} + \text{NaOH(s)} \rightarrow \text{H}_2\text{O} + \text{NaCl(aq)}$ . The second reaction was  $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{H}_2\text{O} + \text{NaCl(aq)}$ . In the second reaction, the neutralization occurred. In the first reaction, the NaOH was separated into  $\text{Na}^+$  ions and  $\text{OH}^-$  ions and the neutralization occurred. The separation of the  $\text{Na}^+$  and  $\text{OH}^-$  ions requires energy. But the formation of hydration bonds when water molecules associate with the ions is exothermic. Overall, the dissolution of NaOH is an exothermic process. We measure the heat by monitoring the temperature change associated with dissolving solid sodium hydroxide in pure water. If we add the heat produced by dissolving the solid NaOH to the heat produced by the neutralization reaction, we find that it is exactly equal to the heat associated with the first reaction.

$$-10.63 \text{ kcal/mol} + -13.35 \text{ kcal/mol} = -23.98 \text{ kcal/mol}$$

This is an example of Hess's law. Hess's law says the sum of the heats associated with the steps in an overall reaction is always exactly equal to the heat associated with the overall reaction when it occurs in one step. Hess's law turns out to represent something significant if we recast it in terms of the enthalpy, rather than the heat associated with the reaction. Note that all three of these reactions occurred in solution under conditions where the pressure was constant. The heat measured for each of the reactions is therefore equal to the enthalpy of each of the reactions. There might be a way for us to extract work from this system, even though no gas is generated. If we could figure that out, the heat associated with the process would be different when we extract work than when we don't. But the amount of enthalpy converted during the reaction would not have changed. The amount of energy converted would not have changed, either. Enthalpy and energy are called "state functions." That means that as long as we start and end two processes at the same conditions, no matter whether we extract work or not, the enthalpy changes and energy changes are the same.

Heat and work are called path functions. We have seen that the amount of work a chemical transformation does can be different if we conduct it in a rigid container or a piston container. Both  $q$  and  $w$  can change depending on the specific manner in which we conduct a chemical transformation. But it is always true that the sum  $q + w$  equals the change in energy,  $\Delta E$ , of the chemical transformation.

## For Greater Understanding

### Questions

1. A particular chemical transformation releases 21 kJ of heat to its surroundings and does 12 kJ of work on its surroundings. What is the energy change associated with the chemical transformation?
  - a. -33 kJ
  - b. -9 kJ
  - c. +9 kJ
  - d. +33 kJ
2. Which of the following reactions could produce pressure-volume work?
  - a. The reaction between baking soda and vinegar, producing carbon dioxide gas.
  - b. The reaction of magnesium metal and hydrochloric acid, producing hydrogen gas.
  - c. The combustion of octane in oxygen, producing carbon dioxide and water gas.
  - d. All of the above.
3. Consider the following enthalpy data:  
 $\text{KOH(s)} \rightarrow \text{KOH(aq)} \quad \Delta H = -57.61 \text{ kJ/mol}$   
 $\text{KOH(s)} + \text{HBr(aq)} \rightarrow \text{H}_2\text{O} + \text{KBr(aq)} \quad \Delta H = -113.45 \text{ kJ/mol}$   
What is the molar enthalpy associated with the reaction  
 $\text{KOH(aq)} + \text{HBr(aq)} \rightarrow \text{H}_2\text{O} + \text{KBr(aq)}$ ?
  - a. -171.06 kJ/mol
  - b. -55.84 kJ/mol
  - c. +55.84 kJ/mol
  - d. +171.06 kJ/mol

### Suggested Reading

American Chemical Society, and Jerry A. Bell. *Chemistry: A General Chemistry Project of the American Chemical Society*. New York: W.H. Freeman, 2005.

Pauling, Linus. *General Chemistry*. New York: Dover Publications, 1988 (1970).

### Other Books of Interest

Atkins, Peter W. *The Laws of Thermodynamics: A Very Short Introduction*. Oxford University Press, USA, Oxford UK, 2010.

Cobb, Cathy. *Magick, Mayhem, and Mavericks: The Spirited History of Physical Chemistry*. Amherst, NY: Prometheus Books, 2002.

Von Baeyer, Hans Christian. *Warmth Disperses and Time Passes: The History of Heat*. New York: Modern Library, 1999.

## Lecture 9

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### Entropy

The Suggested Readings for this lecture are the American Chemical Society and Jerry A. Bell's *Chemistry: A General Chemistry Project of the American Chemical Society*, chapter 8: "Entropy and Molecular Organization," and Linus Pauling's *General Chemistry*.

Neither the energy nor enthalpy change associated with a chemical process predicts whether it happens or not. Some endothermic and some exothermic reactions happen spontaneously. We have discussed the rapid reaction  $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{H}_2\text{O} + \text{NaCl(aq)}$  and combustion, both of which release energy to their surroundings as they proceed. However, we have also described the use of the dissolution of saltpeter to chill drinks centuries before electrical refrigeration was invented.

You may be familiar with the informal statement—"disorder always increases." But this doesn't appear true—precipitates form when solutions are mixed, snowflakes form in winter storm clouds, and living things build highly organized structures. In this lecture, we'll examine the details that make the second law of thermodynamics the measure of which chemical processes happen, and which do not.

Let's start by discussing mixing. If you are at home, you can conduct a little mixing experiment. Half fill a glass with some water. Add one drop of food coloring to the water. What happens? At first, you should be able to differentiate the dye from the water. But if you wait for a while, the dye gradually disperses until it is uniformly distributed throughout the water. This mixing results from the constant, random motion of liquid molecules. Interestingly, however, no matter how long you wait, a uniformly mixed dye will never reparate from the water. The mixing of dye in water illustrates the formal meaning of the word *spontaneous* in science. It is different from your casual use of the word *spontaneous*. A spontaneous chemical process is one that will happen, maybe not instantaneously, but eventually. A nonspontaneous process, like the unmixing of dye and water, will never happen on its own. This doesn't mean we can never separate the dye from the water. It means specifically that if we keep the temperature and pressure the same as they are when the dye and water mix, and if we don't add anything else to the solution that results, then the dye will never spontaneously separate from the water. It means mixing is a one-way road.

Let's consider another kind of mixing, osmosis. Osmosis is an important phenomenon. It is essential to keeping living things alive. Osmosis occurs when two solutions of different concentrations are separated by a semipermeable membrane. Semipermeable membranes often look pretty much like plastic wrap. They are thin and flexible. They are called semipermeable because some molecules are able to pass through them, but others are not. In biology, the most important semipermeable membranes allow water or oxygen

through, but not much else. Sometimes cell walls act as semipermeable membranes. Sometimes synthetic polymers are used instead. Unfortunately, the plastic wrap in your kitchen is specifically made to be impermeable to both oxygen and water, so it's not able to demonstrate osmosis.

In the classic laboratory demonstration of osmosis, you take a bag made of a semi-permeable membrane and fill it with a highly concentrated sugar solution—perhaps one made by mixing one cup of water with one cup of sugar. You place a straw or glass tube into the bag and seal the bag tightly against it. Then you suspend the bag in a beaker of pure water. Almost immediately, the level of the solution in the straw will start to go up. You will need a very tall straw to see where the solution level stops. If your straw is not tall enough, the solution will just flow out the top of the straw, as if you had made an antigravity machine. But, if it is tall enough, eventually the water level in the straw will stabilize. Why does this happen?

One explanation used in introductory chemistry classes goes like this—on a molecular level, the water on the sugar solution side of the membrane competes with the sugar molecules for contact with the membrane. Molecules must be in contact with the membrane in order to move through it. Initially, more water molecules can move from the pure water to the sugar solution than can move in the opposite direction. The solution level on the sugar solution side goes up, and the water level on the water side goes down. As the volume of the solution increases, it begins to exert a pressure on the sugar solution side of the membrane. Because of the straw, this pressure is evidenced by the change in height of the solution, rather than by expansion of the bag. As the pressure on the sugar solution side increases, it pushes the water molecules in the solution more strongly against the semipermeable membrane. The rate at which water molecules are moving from the sugar solution to the water goes up, and the rate at which water molecules are coming from the pure water into the solution goes down. Eventually, water molecules are moving in both directions across the membrane at the same rate, and the height of the solution in the straw stabilizes. At this point, the pressure exerted by the height of the sugar solution above the level of the water is called the osmotic pressure of the solution.

There is a more sophisticated and more generally applicable way to look at the mixing of dye in water, or the establishment of the osmotic pressure, and that is what we really want to consider in the rest of our discussion in this lecture.

Let's recast this discussion in terms of probabilities. When you roll two dice you have a higher probability of rolling a seven than a three, because there are more ways to arrange the dice to give a total of seven dots on top. In the same way, in a chemical system, the number of ways that the molecules and energy in the system can be arranged tells the probability that the system will be observed in that state. Since chemical systems like a cup of water with a drop of food dye added contain huge numbers of molecules, let's first consider an example we can actually count. Once we see the principle, we can extend it to a real chemical sample.

Assume we have three pieces of candy and a box with five compartments. How many different ways could we fill the box? Only one piece of candy can go in each compartment. We can label a compartment with a candy “1” and a compartment without a candy “0.” One arrangement of the candy in the box is (1-1-1-0-0), another is (1-1-0-1-0). If you work through all the possibilities, you will see that there are ten different arrangements of the candies. We say that “W”—the number of ways of arranging the candies in the box—is ten.

If instead of five compartments, we have a box with six compartments, there are twenty ways to distribute our three pieces of candy. If we have seven compartments, there are thirty-five ways to distribute the candies. In eight compartments, the three candies can be arranged in fifty-six ways. The more compartments, the more possible arrangements. You can calculate the number of ways to arrange any number of candies in any number of boxes using a standard statistical formula:

$$W = N!/(N-n)!n!$$

N is the number of compartments, and n is the number of objects to be placed in the compartments. The factorial sign “!” means that you multiply the number by all the integers smaller than it. For instance: “2!” is  $2 \times 1 = 2$ ; “3!” is  $3 \times 2 \times 1 = 6$ ; “10!” is 3,628,800.

Let’s go back to our dye in water example. Let’s assume that in a specific instance, the dye molecules do not mix with the water. If we drop ten molecules of dye in ninety molecules of water, and they don’t mix, there is really only one arrangement for the system. The dye molecules stay in their boxes, and the water molecules stay in theirs. But if the dye molecules can occupy any of the one hundred boxes, the number of ways of arranging the system becomes  $100!/(100-10)! 10! = 17,300,000,000,000$ . That’s 17.3 trillion arrangements.

Of course, real samples of macroscopic size contain many more than ninety molecules of water and ten molecules of dye. For example, 10 mL of water contain  $3 \times 10^{23}$  molecules. So in real samples, the totally mixed scenario has even a higher probability than in this sample of one hundred molecules.

Based on the number of possible ways of arranging things, we find that the better mixed system is always more probable than the highly ordered system. Based on the mathematical probabilities, we predict that chemical systems spontaneously move in the direction of the most probable arrangement of their components. This principle describes why perfume molecules move across the room when you open a perfume bottle, why gas molecules escape from a balloon when it springs a leak, and why the soluble dye molecules disperse when dropped in water.

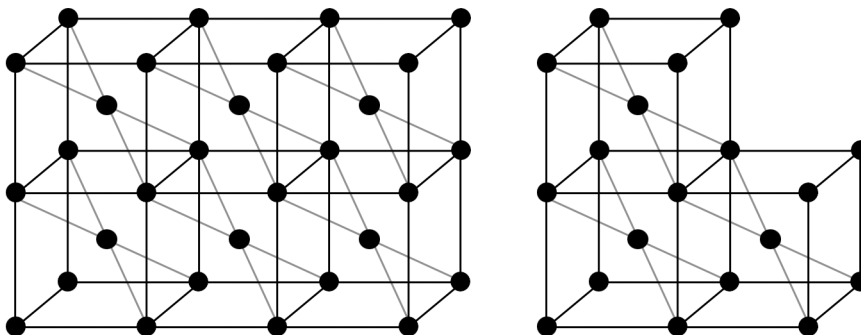
We have seen that energy is an important aspect of chemical transformations. Let’s consider the ways to distribute energy in a chemical system. Recall that energy is quantized. In our calculations here, we will identify the number of quanta of energy present, as that is an easier way to count the energy distributions. Consider a solid of four

atoms with four quanta of energy. How many ways can the energy be distributed? We can run through several options fairly quickly. The four quanta could be distributed such that all four energy quanta were on one atom. There are four different ways to do this. Or the energy could be distributed so that one quantum was on each of the atoms. There is one way to do this, or there could be two atoms with one quantum of energy, and one with two. There are twelve ways to distribute the energy in that pattern. Or there could be two quanta on two atoms. There are twelve ways to do that. Or there could be three on one and one on another. There are twelve ways to do that. Interestingly, it is more likely that this system will have two quanta on two molecules than that all the molecules will have one quantum of energy. As more quanta are added to the system, the number of ways to arrange the quanta increases dramatically.

Consider that we have two identical four-atom solids, one with two quanta of energy and one with six. The number of ways to organize the system of two solids is the number of ways to arrange solid one times the number of ways to arrange solid two. There are ten ways to arrange two quanta of energy in a solid of four particles:  $2-0-0-0 =$  four ways;  $1-1-0-0 =$  six ways. With six quanta, there are eighty-four ways to arrange the quanta. The total number of possible arrangements of energy in the two solids is  $10 \times 84 = 840$ .

If we put the two solids in contact, what happens? If the quanta stay where they are, nothing happens. But if the quanta can be exchanged, we find that moving two quanta from the six-quantum body to the two-quantum body gives us thirty-five ways to organize the quanta in each solid. In total, then, there are  $35 \times 35 = 1,225$  ways to organize the quanta. The equal arrangement of the quanta is the most probable arrangement. This is another way of saying that a hot object and a cold object put in contact will spontaneously come to the same temperature.

In macroscopic-sized systems, the number of possible ways to arrange energy quanta can become huge. We can define the entropy as being a measure of the ways the energy can be arranged in a chemical system. The more ways, the higher the entropy. The formal mathematic definition of entropy is  $S = k \ln W$ .



In solids, changing the volume changes the number of atoms or ions AND the volume.  
The concentration is always the same, no matter how large or small the sample.

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The  $k$  represents the Boltzmann constant. Although named for Ludwig Boltzmann (1844–1906), the numerical value of the constant was first derived by Max Planck during his studies to explain black-body radiation. The average energy of a collection of atoms is described by a temperature and is proportional to  $k$ . The average energy of a mole of Ar gas at temperature ( $T$ ) is  $(3/2)kT$ , for example. Here  $T$  is measured on the absolute temperature scale, using absolute 0 as 0 K (and  $0^{\circ}\text{C}$  as  $273.15^{\circ}\text{K}$ ). If you multiply  $k$  by  $N$ , Avogadro's number, you get the gas constant  $R$  that we also derived from the  $PV/Tn$  ratio of any ideal gas sample. Boltzmann's constant has units of J/K.  $R$  has units of J/K-mol.

The symbol “ln” refers to the mathematical operation called the natural logarithm. Natural logarithms operate in the same way as base-10 logarithms, but they use a different base number. Natural logarithms use the base  $e = 2.718281828$ , a transcendental number reported here to ten significant figures. Just as in our discussion of pH, we defined that if  $y = 10^x$  then  $\log y = x$ ; here we define that if  $y = e^x$ ,  $\ln y = x$ . In the modern era, natural logs are simply a button (ln) on our calculators. Mathematicians called this function the natural log because it arose naturally in mathematics. The  $\ln(a)$  is defined as the area under the graph of  $1/x$  from 1 to  $a$  and is therefore frequently encountered in calculus, where finding the area under a graph is equivalent to integration.

But back to chemistry. In any chemical transformation, the net entropy change is the sum of all the entropies after the transformation compared to the total entropies before. The second law of thermodynamics says spontaneous changes are always accompanied by a net increase in entropy. Since the entropy is related to temperature, and we know there is an absolute zero temperature, it turns out that we can define an absolute entropy for any system. Remember that energy and enthalpy are always reported as the difference between a particular situation and a defined standard state. But entropy can be assigned an absolute scale. We say the entropy of a perfect crystalline solid approaches zero as the absolute temperature approaches  $0^{\circ}\text{K}$ . Note that an entropy of 0 means that there is only one way to arrange the energy of the system, since  $S = k \ln W$ .

Let's apply this idea of entropy to consider phase changes. Since water is the compound that can undergo these phase transitions under conditions with which we are familiar, let's consider water. When water molecules are solid, they have a regular three-dimensional arrangement and are fixed in space relative to one another. The solid is rigid. Its atoms are confined to one configuration. From a positional standpoint, its entropy is zero. If we add heat to the solid water, we can melt it into a liquid. In liquids, the atoms occupy their own volume but are free to move around within that volume. Liquids have a much higher entropy than solids. The same sample of water evaporated into a gas will occupy a much greater volume than it did as a liquid. The molecules in a gas have an enormous number of ways to organize. According to the positional entropy, everything should want to be a gas. Nevertheless, we are surrounded by solids and liquids. What have we missed?

Of course, we need to consider the energy distribution in addition to the positional entropy. Since moving from solid to liquid to gas requires the addition of heat to the substance, we

know that the thermal entropy of the substance will increase as it undergoes this series of transitions, too. From an entropy standpoint, it seems that everything wants to be a gas.

But wait. There's a glitch. If heat flows into a system containing solid ice, and warms it, the same energy must have left the surroundings of the ice. The transition has definitely cost the surroundings some entropy; therefore, it appears we need to consider both what happens in the system and what happens in the surroundings to determine whether or not a transformation is spontaneous.

If you think about it, adding or subtracting energy from the surroundings affects the energy of the surroundings in a way that is inversely proportional to the surrounding temperature. If the surroundings are really hot, taking a little energy from them won't make much change in the entropy. But if the surroundings are cooler, taking the same amount of heat from it will have a much larger effect. For a transformation that occurs at constant pressure, which is our normal experience of the melting of ice or boiling of water, we have seen that  $q$ , the heat transferred, equals  $\Delta H$ , the enthalpy change of the system. The heat transfer affects the entropy according to the equation  $\Delta S = \Delta H/T$ .

A specific example is in order. Take 18 g of ice at  $0^{\circ}\text{C}$  and place the ice in an environment where the temperature of the surroundings is  $-5^{\circ}\text{C}$ . Then move the same sample to a place where its surroundings have a temperature of  $+5^{\circ}\text{C}$ . If the ice is going to melt, we have to provide heat to break some of the intermolecular forces so the water becomes a liquid. Does this happen spontaneously? The heat of fusion of ice (the energy to melt it) is  $6.00 \text{ kJ/mol}$ . The entropy change accompanying the conversion of solid ice to water is  $22.0 \text{ kJ/mol}\cdot\text{K}$ . So the question is, when is the conversion spontaneous?

At  $-5^{\circ}\text{C}$ , the  $6 \text{ kJ}$  of heat provided to the solid from the surroundings means that the surroundings experience a decrease in entropy of  $-6.00 \text{ kJ}/268^{\circ}\text{K} = -22.4 \text{ kJ/mol}$ .

The entropy increase when the solid is converted to a liquid is  $+22.0 \text{ kJ}$ . The total entropy change of both the system and its surroundings is  $-0.4 \text{ kJ/mol}$ . Therefore, this reaction does not happen at  $268^{\circ}\text{K}$ .

What about at  $278^{\circ}\text{K}$ ? Now the entropy decrease in the surroundings is  $-6.00 \text{ kJ}/278^{\circ}\text{K} = -21.5 \text{ kJ/mol}$ . The entropy change of the ice is  $22.0 \text{ kJ/mol}$ . So at  $278^{\circ}\text{K}$  the total energy change of the universe is  $+0.5 \text{ kJ/mol}$ . When the surroundings are at  $278^{\circ}\text{K}$ , the melting of ice is spontaneous.

You already knew this, of course. But this example demonstrates how the second law gives us the full picture of whether transformations are spontaneous or not. But having to keep track of the surroundings is a pain in the neck. We would much prefer to focus on the system only.

To focus on the system, we need to introduce a new thermodynamic function, the Gibbs free energy,  $\Delta G$ . The Gibbs free energy is defined as follows:

$$\Delta G = \Delta H - T \times \Delta S$$



How does the Gibbs free energy allow us to focus on the system and avoid worrying about the surroundings? Let's begin with a mathematical statement of the entropy changes associated with a spontaneous chemical process.

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{universe}}$$

We have already established that the  $\Delta S_{\text{surroundings}}$  is calculated by reversing the sign on the  $\Delta H$  of the system and dividing by the temperature. So  $\Delta S_{\text{surroundings}} = -\Delta H_{\text{system}}/T$ .

$$\text{Then } \Delta S_{\text{universe}} = \Delta S_{\text{system}} - \Delta H_{\text{system}}/T.$$

If we multiply through by the temperature, we get the following:

$$T \times \Delta S_{\text{universe}} = T \times \Delta S_{\text{system}} - \Delta H_{\text{system}}$$

And then we get this:

$$-\Delta G_{\text{system}} = T \times \Delta S_{\text{universe}}$$

Because we are using temperature in degrees K, the temperature of any system is always positive. Therefore, when the  $\Delta S$  of the universe increases, as required for a spontaneous process, the  $\Delta G$  of the system is negative. But either measure predicts whether or not a process is spontaneous. The advantage of  $\Delta G$  is that we only need to consider the system.

Why is  $\Delta G$  called the Gibbs free energy? What's free about it? Entropy takes account of the molecular rearrangements that happen during transition. But the free energy is available to do work in the surroundings. When we want to use a chemical reaction to do work, the Gibbs free energy tells us how much work the transformation can do under optimal conditions.

Most chemistry books have tables of experimentally determined thermodynamic properties for compounds in their standard states. The tables allow chemists to determine whether or not specific reactions should be spontaneous and to calculate the enthalpy and free energy associated with the transformation if it happens.

## For Greater Understanding

### Questions

1. In chemistry, the word *spontaneous* describes a transformation that
  - a. occurs immediately with the release of energy from the system.
  - b. occurs immediately, but the system could release or absorb energy.
  - c. occurs eventually without any external interference.
  - d. occurs eventually if you provide heat to the system.
2. Which of the following statements is true?
  - a. One mole of solid NaCl and 2 L of water have a higher total entropy than a system consisting of one mole of NaCl dissolved in 2 L of water.
  - b. One mole of copper at 300°K has a higher entropy than one mole of copper at 273°K.
  - c. One million molecules of methane, CH<sub>4</sub>, confined to a 1 microliter container at 300°K will have a higher entropy than one million molecules of CH<sub>4</sub> confined to a 5 microliter container at the same temperature.
  - d. One gram of copper metal has a higher entropy than one gram of silver metal at the same temperature.

### Suggested Reading

American Chemical Society, and Jerry A. Bell. *Chemistry: A General Chemistry Project of the American Chemical Society*. New York: W.H. Freeman, 2005.

Pauling, Linus. *General Chemistry*. New York: Dover Publications, 1988 (1970).

### Other Books of Interest

Ben-Naim, Arieh. *Discover Entropy and the Second Law of Thermodynamics: A Playful Way of Discovering a Law of Nature*. Singapore: World Scientific Publishing, 2010.

Von Baeyer, Hans Christian. *Warmth Disperses and Time Passes: The History of Heat*. New York: Modern Library, 1999.

## Lecture 10

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### Kinetics

The Suggested Readings for this lecture are the American Chemical Society and Jerry A. Bell's *Chemistry: A General Chemistry Project of the American Chemical Society*, chapter 11: "Reaction Pathways," and Linus Pauling's *General Chemistry*.

In the last lecture, we described spontaneous reactions. But we haven't yet talked about how fast those spontaneous reactions are. In this lesson, we will look at the factors that affect reaction rates and the mathematical formalism used to describe chemical kinetics.

First let's consider the range of reaction rates with which we are familiar. An explosion is a very fast, usually exothermic, reaction. The airbag in your car is inflated when sodium azide, a solid, is converted to nitrogen gas. This reaction produces almost no heat. All the excess energy goes into translational motion of the nitrogen gas. This inflates your air bag in the fraction of a second it takes your body to collide with your steering wheel.

On the other end, some reactions are really slow. For example, the conversion of diamond to graphite is spontaneous under normal temperature and pressure conditions. But this reaction is so slow that no one has seen this reaction actually occur, much to the relief of diamond lovers everywhere. Our discussion of kinetics will begin with a formal definition of the rate of a reaction and then continue by identifying those conditions that speed up these slow reactions.

We define the speed of a reaction in a manner similar to the way in which we define the speed of a car. A car is moving down the highway, and you want to know how fast it is going. How do you measure its speed? If you are in the car, you can just look at the speedometer. If you are a highway patrol officer, you can consult your radar gun. But if you are a casual observer on the side of the road, and you have a stop watch, you can determine the speed if you know how far apart two points on the road are and you measure the time it takes for the car to travel between the two points:

$$\text{Speed} = \text{velocity} = \text{rate} = \text{change in position/change in time} = \text{distance/time}$$

The study of the speed, velocity, or rate of chemical reactions and the factors that affect them is called kinetics.

In chemical reactions, in lieu of measuring the position, we measure the concentration of one of the reagents or products in the reaction and watch it change over some period of time in order to determine the rate of the reaction. The way in which we measure the concentration is often determined by the properties of the reagents and products in the reaction.

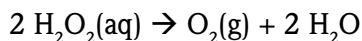
We have discussed the use of indicator dyes for detecting the amount of acid or bases present in aqueous solutions. If you add one drop of a dilute solution of phenolphthalein

to a solution of sodium hydroxide, you will immediately see a bright pink color develop where the drop meets the solution. The reaction in which the phenolphthalein transfers two protons to the hydroxide, forming water and yielding a doubly charged and rearranged product that is bright pink, happens essentially as quickly as the collisions between the hydroxide and the phenolphthalein molecules collide.

If you keep watching the bright pink dot for a while, however, its color will fade away. It appears that a secondary reaction is occurring. Two quick experiments using a more concentrated and a less concentrated solution of sodium hydroxide shows that the fading happens more quickly when the concentration of sodium hydroxide is higher. These observations are consistent with the relatively slow formation of a triply negative, rearranged product, which does not share the color of the product from the first step in the reaction. These observations indicate that the concentration of a reagent can affect the rate of a reaction.

If you cook, you know that the time it takes to bake bread can vary depending on the temperature of your oven. The hotter the oven, the less time it takes to turn dough into bread. Baking is applied chemistry. In fact, almost all reactions go faster at higher temperatures. We know that increasing temperature increases the energy of a chemical system, so this observation leads us to conclude that the temperature or energy of the reagents is a factor in determining how fast a reaction is.

In your medicine cabinet, you might have a bottle of hydrogen peroxide. My mother-in-law used peroxide to treat the many cuts her three boys got regularly while growing up. What does peroxide do? In your cabinet, not much. It lasts for a year or so, as long as the bottle stays closed. But open it up and pour it on a cut and it quickly generates lots of bubbles. The peroxide,  $\text{H}_2\text{O}_2$ , decomposes, forming oxygen gas and leaving water behind.



If you expose the peroxide to almost any biological product, a piece of apple, raw potato, raw beef, or a drop of blood, it immediately begins to form bubbles, which it does not do at any noticeable rate when the biological samples are not present. In this example, the biological material is said to *catalyze* the reaction.

This set of observations provides us with a framework for systematically studying reaction kinetics. Among the factors we will need to consider are the temperature of the reagents, the concentration of the reagents, and the presence of catalysts.

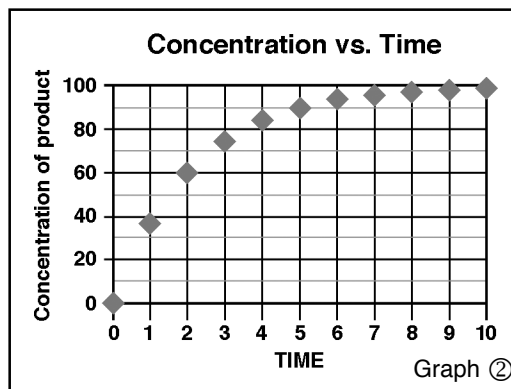
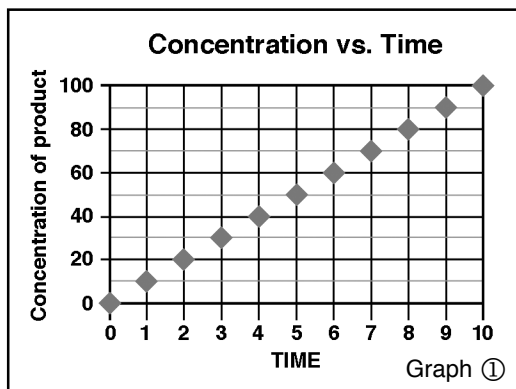
The method used to measure the rate of a chemical reaction must be customized to the reaction being studied. To examine the kinetics of the fading of the phenolphthalein  $-2$  anion intermediate above, we could employ optical spectroscopy. The red species preferentially absorbs green light. We can correlate the amount of light absorbed with the concentration of the pink species. In this way, we could measure the concentration of the phenolphthalein  $-2$  over time and determine the rate at which it changes.

The peroxide decomposition is not correlated with a color change. Therefore, we can not use visible spectroscopy to monitor it. But the reaction does produce a gas. If we have a pressure gauge and conduct the reaction in a container strong enough to contain the pressure change, we can use the pressure change to measure the amount of gas formed over some period of time, and also determine the rate of the reaction.

Let's be a little bit careful here. If we measure either the optical absorbance of the phenolphthalein or the pressure of the gas, we are measuring the amount of product present at specific times after the reaction has begun. To find the rate of the reaction, we need to determine how the amount of product present changes over some period of time. In the two examples here, the product is confined to a specific volume, the volume of the solution in the case of the phenolphthalein, and the volume of the gas container in the case of the peroxide. When the volume is fixed, chemists generally report the concentration of the product, rather than its absolute amount. So we define the rate of a chemical reaction as the change in concentration over the change in time:

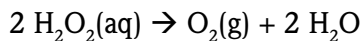
$$\text{rate} = \Delta \text{ concentration} / \Delta \text{ time}$$

Sometimes a picture is worth a thousand words. Here are two typical graphs for how concentration changes over time in chemical reactions:



A mathematician would say that the rate of the reaction is the slope of the line of concentration vs. time or the derivative of the concentration vs. time. The units on the reaction rate might be defined as kilopascals per second (kPa/sec) or atmospheres/hour or Molarity/min, depending on the way in which the product concentration was measured and the time the reaction takes.

Since we are focusing on the products in these examples, the rate of the reaction is positive. Chemists prefer that the rate of the reaction be reported as the same value whether they are considering the formation of a product or the consumption of a reagent to determine it. The stoichiometry of the reaction is therefore related to the way in which the rate is expressed. The decomposition of hydrogen peroxide is expressed as follows:



The peroxide gets used up twice as fast as the oxygen is formed. We prefer to identify the rate of the reaction by one positive number, however. So we use the stoichiometry of the equation to mathematically define the rate of the reaction:

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta\text{time}} = +\frac{1\Delta[\text{O}_2]}{1\Delta\text{time}}$$

Note that the pressure of the oxygen gas increases over time, and the amount of peroxide goes down twice as fast. So if we define delta as referring to a later time minus an earlier time, the addition of the minus sign in front of the reagent behavior means that we always define reaction rates to be positive. The factor of one-half corrects for the two-to-one stoichiometry.

When we actually perform an experiment to measure the rate of the peroxide decomposition, we observe that at first, the pressure appears to increase linearly in time. But eventually the rate of production slows down, and the pressure versus time curve begins to turn over and approach a horizontal limit. This behavior is described by the graph on the right. Clearly the rate of the reaction is changing as it proceeds. If we graph the actual data, we can find the average rate of the reaction over any time period by finding the slope:

$$\text{Rate} = \text{slope} = +\frac{1}{1} \frac{P(\text{time } 2) - P(\text{time } 1)}{\text{time } 2 - \text{time } 1}$$

The fact that the rate changes as the reaction proceeds is consistent with our early assertion that the concentration of the reagents can affect the rate of the reaction. Although it is possible to perform a mathematical analysis to determine exactly how the concentration of the reagents affects the rate of the reaction, it is typical in laboratory settings to employ an experimental approach called the method of initial rates to examine the effect of both concentration and temperature on reaction rates. In the method of initial rates, we choose a time window over which the reaction of interest appears to behave linearly, and we keep that time window constant throughout the experiment. In an initial rate study of peroxide decomposition, we can examine the effect of changing peroxide composition by keeping the concentration of the catalyst and the temperature constant while systematically changing the concentration of peroxide with which we begin the reaction. If we always measure the pressure of the oxygen gas produced one minute after the reaction begins, we can examine the effect of peroxide concentration on the decomposition rate. In the lab, near room temperature, we find that doubling the peroxide concentration doubles the pressure of the oxygen gas produced at one minute and that halving the concentration of peroxide halves the pressure of the oxygen gas produced at one minute. Calculating the rate from the equation above, we see that the rate doubles when the concentration doubles. If we make a graph of the rate of production of oxygen gas (in atm/min) versus the concentration of peroxide (in mole/L), the graph is linear.

Since the catalyst is required for the reaction to proceed at a rate we can monitor in the lab, we can measure the effect of its concentration on the reaction rate, too. There is an art to setting up kinetics experiments. The results reported about the effect of changing the peroxide concentration can be obscured if an inappropriate amount of catalyst is present. The effect of the catalyst can be obscured if the amount of reagent, or the time window or the pressure measurement, is not appropriate. Here, we are quoting ideal results. Ideal results are only obtained after considerable effort to understand the kinetics has already been undertaken. Under these ideal conditions, doubling the amount of catalyst present doubles the rate of the reaction.

Either of these results, the effect of the peroxide concentration or the catalyst concentration on the rate of the decomposition, can therefore be described by a linear equation,  $y = mx + b$ . Here  $y$  = rate,  $x$  = concentration,  $k$  = slope of the line, and in both cases cited here,  $b$  is zero, because the reaction does not happen if there is no peroxide, nor does it proceed without some catalyst present.

From the results of our initial rate law experiment, we can write a rate law: rate =  $k$   $[H_2O_2][catalyst]$ . For a particular catalyst we might find that at 25°C, the  $k$  for the peroxide decomposition is  $8.3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ .

In the terminology of kinetics, when the graph of rate versus concentration is linear, we say that the decomposition is “1<sup>st</sup>” in peroxide, first order in the catalyst and second order overall.

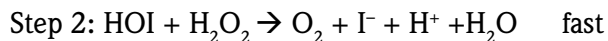
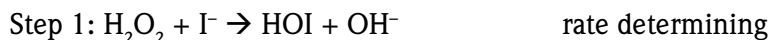
Note that the rate law is determined experimentally. Note that the catalyst is not included in the reaction stoichiometry, but it does appear in the rate law. This emphasizes that rate laws are always experimentally determined and do not have any necessary relationship to the stoichiometry of the reaction.

Kinetics are important, but the real insight of kinetics is when it reveals not just how fast reactions occur, but the mechanisms by which they occur. We already have an indication that the reaction between phenolphthalein and hydroxide ion occurs in steps. In fact, most reactions occur in stepwise fashion.

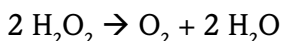
When a reaction proceeds in steps, there is always one step, the rate-limiting step, which controls the speed of the overall reaction process. Just as in any baking or manufacturing process, in chemistry there is one step that is slowest and therefore limits the rate at which you can produce products.

If we catalyze the decomposition of peroxide near room temperature by adding iodide ion, how does the decomposition proceed? Since the rate law is first order in iodide ion and first order in  $H_2O_2$ , it is reasonable to assume that the rate limiting step involves a collision and reaction between these two species. In our previous discussions, we have seen that the formal charge on an O in  $H_2O_2$  is  $-1$ , but we know that oxygen is more stable when its oxidation state is  $-2$ . A reasonable mechanism for the rate-determining

step in the reaction might be that the  $\text{I}^{-1}$  attaches to one of the O's and transfers electrons to it, causing the O-O bond to break, producing HOI and  $\text{OH}^{-}$  as intermediates. Other steps are required to achieve the observed overall stoichiometry.



The overall reaction is determined by adding all the reagents and all the products and cancelling out the species that are not changed in the course of the reaction. In this case, the result of this fun chemistry math is as follows:



This series of steps is simply a hypothesis until the intermediates, in this case HOI and  $\text{OH}^{-}$ , are detected and monitored in the reaction. Molecular dynamics is the name given to tracking down the intermediates proposed in reaction mechanisms.

So far we have only discussed first-order reactions. Most introductory chemistry classes are concerned with three orders of reactions, zeroth order, first order, and second order. Our more formal mathematical discussion begins with first things first.

In addition to the decomposition of peroxide, all radioactive processes are first order. The rate of the reaction is directly related to the number of nuclei present. Since the number of nuclei is decreasing over time the rate  $-\Delta N/\Delta t = k \cdot N$  is decreasing, too. If we rearrange this equation to  $-\Delta N/N = k \Delta t$  and choose any time interval, the right-hand side is constant. For first-order reactions, this says that the fraction of reagents that react in a given period of time is the same no matter how many reagent molecules you have. You can easily make a graph to illustrate this behavior. Mark the x-axis in multiples of  $\Delta t$ , 1, 2, 3, 4 . . . The marks should be evenly spaced across the axis to indicate that delta t is being held constant. Mark the vertical axis to show N. Since we know any reasonable-sized sample will contain millions of nuclei, you can choose any appropriate large number for the max on the y-axis. For the sake of illustration, let's choose to start the thought experiment with 100,000 nuclei.

According to the first-order kinetics, the fraction of the nuclei that decay is the same over each interval delta t. Let's assume that in this case one-fifth of the nuclei decay in delta t. Then 20,000 nuclei decay between  $t = 0$  and  $t = 1$ , so at  $t = 1$ , 80,000 nuclei remain. Between  $t = 1$  and  $t = 2$ ,  $1/5 \cdot 80,000 = 16,000$  nuclei decay leaving  $80,000 - 16,000 = 64,000$  nuclei at  $t = 2$ . In the next interval, 12,800 decay, leaving 51,200 nuclei at  $t = 3$ . You can continue this calculation as long as you like. The table of data and a graph of nuclei remaining as a function of time are shown on the following page.



Table of Radioactive Nuclei Decaying Over Time

t	# nuclei	$\Delta$ nuclei
0	100,000	20,000
1	80,000	16,000
2	64,000	12,800
3	51,200	10,240
4	40,960	8,192
5	32,768	6,554
6	26,214	5,243
7	20,971	

A graph of N versus time gives a smooth curve that decreases more and more slowly as time increases. It looks like the side of a volcano. Since it shows the concentration of reagents over time, instead of the concentration of the products, it is inversely related to Graph 1 on page 100. A graph of the slope  $\Delta N$  versus time gives the rate versus time. This graph shows the same curved relationship between rate and time. The graph of N versus time shows an integrated rate law for the radioactive decay. The graph of the rate versus time shows a differential rate law for the radioactive decay.

The curved behaviors on the graphs are characteristic of logarithmic behavior. If you take the natural log of N and plot it versus t you get a straight line graph with a negative slope (N is the reagent and is therefore decreasing over time) and an intercept,  $\ln(N_0)$ . A linear plot of  $\ln(N)$  versus time is the signature of a first-order reaction. The slope of the line is  $-k$ , where k is the rate constant for the reaction.

We can describe the first-order reaction by the equation:

$$\ln(N(t)) = \ln(N_0) - kt$$

Remember that nuclear decay processes are characterized by a half-life that is independent of the number of nuclei present initially. In this analysis we define the half-life to be the time when half the nuclei have decayed. At  $t_{1/2}$  the equation is as follows:

$$\ln\left(\frac{N_0}{2}\right) = \ln N_0 - kt_{1/2}$$

Rearranging, we get this:

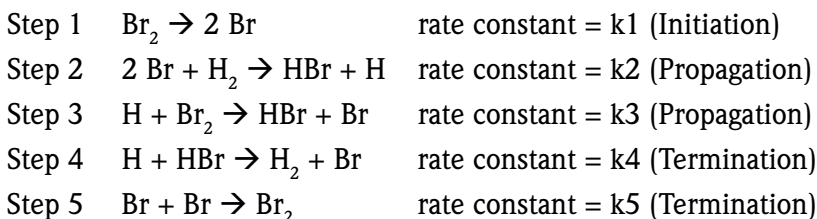
$$kt_{1/2} = \ln N_0 - \ln\left(\frac{N_0}{2}\right) = \ln\left(\frac{N_0}{\frac{N_0}{2}}\right) = \ln 2 = 0.693$$

Therefore,  $t_{1/2} = 0.693/k$ .

In this reaction, the graphs show that the half-life is about three delta t. The math shows that the half-life is  $(0.693/.2231) = 3.11 \text{ t's}$ . Note that both the number of decays/time interval and the actual number of reagent nuclei have both decreased to half their initial values at  $t_{1/2}$ .

The order of the reaction  $\text{H}_2 + \text{I}_2 = 2 \text{ HI}$  has been cited as the archetypical second order reaction since its kinetics were reported in 1894. The reaction is a second-order reaction because it appears that one  $\text{H}_2$  and one  $\text{I}_2$  slam into each other to initiate the direct formation of the products.

The mechanism of the reaction between  $\text{H}_2$  and  $\text{Br}_2$  might reasonably be expected to follow the same mechanism as  $\text{H}_2 + \text{I}_2$ . But, from the earliest studies, it was clear that  $\text{H}_2 + \text{Br}_2 \rightarrow 2 \text{ HBr}$  did not happen through a single collision that formed a four-center transition state. The current understanding of the mechanism is that the reaction occurs in five elementary reaction steps:



Because each of these steps involves a neutral atom with an unpaired electron, a radical, this mechanism is called a radical chain reaction. In general, reaction steps in which radicals combine are fast, and reaction steps in which radicals are formed are slow. However, the specific kinetics observed for this reaction depend on both the temperature and the concentrations of the reagents.

The temperature affects the rate constant  $k$  for each reaction step. We have already asserted that  $k$  increases with temperature. The model we use was first described by Svante Arrhenius in the late 1800s. Arrhenius saw that the natural log of the rate constants for a reaction plotted as a function of  $1/\text{temperature}$  gave a linear relationship.

$$\ln(k) = \ln A - \frac{B}{T} \text{ or } k = Ae^{-\frac{B}{T}}$$

Here  $\ln A$  is the intercept and  $-B$  is the slope of the graph.  $A$  and  $B$  are independent of temperature, but they are different for each reaction studied. Arrhenius connected this mathematical equation with the potential energy diagram for a chemical reaction. If you think of the potential energy diagram, you remember that there is generally a hill that separates the reagents from the products. Arrhenius saw that the constant  $B$  was related to the height of the hill when measured from the reagent side. In order for a reaction to occur, a collision needs to happen to allow the reagents to convert kinetic energy into chemical energy so appropriate bonds can be broken to start the reaction process. The higher

the hill, the smaller the fraction of molecules in any sample that have enough energy to surmount it, and the smaller  $k$ . The  $B$  in Arrhenius's equation is therefore a measure of the activation energy of the reaction.

But energy itself is not sufficient to cause the reaction. Often the orientation of the reagents matters, too. In the mechanisms we have looked at so far, the orientation factor is most easily seen in step 4 of the  $H^2 + Br^2$  mechanism. From a simplistic perspective, if you want an H atom to collide with an HBr molecule and produce an  $H^2$ , you probably will have better luck if the H atom collides with the hydrogen end of the HBr. Otherwise, the H's might exchange the Br, but no reaction step will occur. Of course, hydrogen is small and more likely to follow odd quantum rules than any other atom, but the principle is correct whether the details are or not. The  $A$  in Arrhenius's equation is called the orientation factor. The larger  $A$  is, the more likely any collision orientation is to produce products, and the larger  $k$  and the faster the reaction.

So far, we have considered reactions that proceed in one direction only. But most reactions are actually reversible. In the next lesson we'll examine the consequences of reversible reactions.

## For Greater Understanding

### Questions

1. When a graph of concentration vs. time yields a straight line,
  - a. the rate of the reaction is zero.
  - b. the rate of the reaction is constant and independent of the concentration of the reagent.
  - c. The concentration of the reagent is constant over time.
  - d. The rate of the reaction is equal to the concentration of the reagent.
2. In general, the higher the activation barrier
  - a. the more exothermic the reaction.
  - b. the faster the reaction.
  - c. the slower the reaction.
  - d. the more endothermic the reaction.
3. Consider the reaction  $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$ . When oxygen is being consumed at a rate of 1.6 moles/minute, how fast is carbon dioxide being produced?
  - a. 3.2 moles/minute
  - b. 1.6 moles/minute
  - c. 1.0 moles/minute
  - d. 0.8 moles/minute

### Suggested Reading

American Chemical Society, and Jerry A. Bell. *Chemistry: A General Chemistry Project of the American Chemical Society*. New York: W.H. Freeman, 2005.

Pauling, Linus. *General Chemistry*. New York: Dover Publications, 1988 (1970).

### Other Books of Interest

Laidler, Keith J. *Chemical Kinetics*. 3rd ed. New York: Prentice Hall, 1987.

Shakhashiri, Bassam Z., and Rodney Schreiner. *Chemical Kinetics*. 2nd ed. Champaign, IL: Stipes Publishing Co., 2005.

## Lecture 11

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### Chemical Equilibrium

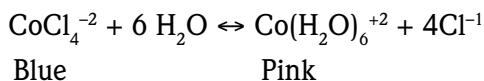
The Suggested Readings for this lecture are the American Chemical Society and Jerry A. Bell's *Chemistry: A General Chemistry Project of the American Chemical Society*, chapter 9: "Chemical Equilibria," and Linus Pauling's *General Chemistry*.

In lecture 9, we saw that systems spontaneously move in the direction that minimizes their Gibbs energy. We say that chemical systems are "at equilibrium" with their surroundings when the Gibbs energy is at a minimum. It is important to realize that chemical processes do not stop when a system is at equilibrium. While an externally measurable quantity, perhaps pressure or concentration, may appear unchanging, in the chemical system, at the molecular level, the behavior is just as dynamic as ever. The molecules continue to react at equilibrium just as they do when the system is not at equilibrium. But at equilibrium, the rate of the reaction that would produce an increase in pressure is exactly the same as the rate of the opposing reaction that would produce a decrease in pressure. There is no change in the total pressure, even though the reaction continues. If the concentration of a product is being monitored, the rate at which the product is being made is the same as the rate at which the product is being converted back to reagents. There is no net change in concentration over time. This is similar to the ideal budgetary situation in our households—when our salaries every month exactly equal our expenses, we have a perfectly balanced, equilibrium budget.

Of course, sometimes chemical systems appear to be at equilibrium because the rate at which they are changing is too slow for us to detect. How can we distinguish slowly changing systems from equilibrium systems? We can see how they respond to a small change. According to Le Chatelier's principle, a chemical system *at equilibrium* acts in opposition to any change we impose on the system. In other words, chemical systems are like obstinate two-year-olds. Whatever you want them to do, they do the opposite.

Lots of labs use anhydrous calcium sulfate as a drying agent. It absorbs water and keeps sensitive samples dry. Sometimes, the calcium sulfate is impregnated with small amounts of cobalt chloride. The cobalt chloride is blue when dry but turns pink when it absorbs water molecules. A systematic study of the color of cobalt chloride is most easily undertaken by dissolving some  $\text{Co}(\text{H}_2\text{O})_6\text{Cl}_2$  solid in rubbing alcohol. The solid is a deep red-purple color but forms a blue solution when dissolved in alcohol. If you add a few drops of water to the solution, however, the color changes to pink. The displacement of the Lewis base  $\text{Cl}^-$  by  $\text{H}_2\text{O}$  is enough to change the electronic environment of the cobalt ion, producing the color change. And the change is completely reversible. Put the calcium sulfate in a humid environment and the water will displace the chlorides from around cobalt and the sample will turn pink. Put the pink stuff in a dry environment, and the waters will evaporate. Their

places will be occupied by  $\text{Cl}^{-1}$  ions and the compound will turn blue. The color is easy to see and will change back and forth as the environment changes. The following is the chemical reaction under consideration:



How does Le Chatelier's principle describe the behavior we observe? Let's say we try to add some extra water to the system. The addition moves the system from an equilibrium state to a state where it is not at equilibrium. The system acts like a two-year-old—*I don't want that extra water!*—so the water gets absorbed by the Co complex, displacing some  $\text{Cl}^{-1}$  and changing the color.

In addition to concentration, we know that temperature affects reaction rates. Does it also affect equilibrium? To investigate this question, we could add just a little water to produce a lavender solution of cobalt chloride in alcohol. If we heat the lavender solution, perhaps by placing it in a hot-water bath, it turns blue. When you remove heat from the same solution, perhaps by placing it in an ice-water bath, it turns red. If you let it return to room temperature, it becomes lavender again. This observation tells us that the  $\text{CoCl}_4^{-2}$  complex is higher in energy than the  $\text{Co}(\text{H}_2\text{O})_6^{+2}$  complex. The reaction we wrote is exothermic, and it releases heat to its surroundings as the energy of the complex decreases and the reaction proceeds in the direction it is written.

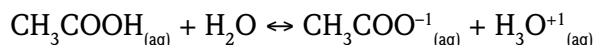
Although the Gibbs energy gives us a clear indication of when systems are at equilibrium, it is a difficult quantity to access in everyday use in the lab. We need a more accessible way to describe equilibrium and decide whether the systems we observe are, or are not, at equilibrium.

Let's consider a dye that changes color when the pH of its environment changes. Such dyes are called indicators. You may have used litmus paper, a paper impregnated with litmus. Litmus paper is a natural product and was originally a compound extracted from lichens. Litmus is red when in contact with acids and blue when in contact with bases. Chemists often use phenolphthalein, another natural product, which is colorless in acidic solutions but pink in basic solutions. The most accessible indicator dyes for the home chemist are from red cabbage. Cut a small head of cabbage into pieces and place the cabbage in a blender. Add enough water to cover and blend briefly. Strain the resulting liquid from the solids. A compound called flavin is easily extracted by the water and changes color depending on its environment—usually it is red in tap water.

You can test the pH of any water-soluble solid, or any clear liquid in your kitchen, by mixing up a batch of red cabbage juice for yourself. Why are we discussing dyes in the middle of a discussion about determining equilibrium? Because of their color changes! The color change provides a built-in way to measure the quantity of dye present in its colored form. If all we want is a rough estimate, we can depend on our vision. If litmus paper turns blue, the solution is basic. How basic? Litmus can't tell us. To know how basic the solution

is, we need to add a dye to a test solution and measure its absorbance to determine the concentration of the colored form of the dye. If we know the total amount of dye we added, we can also determine the amount of dye present in its uncolored form. The concentrations of the dyes give us a window into equilibrium systems.

A common household chemical we could test with cabbage indicator is acetic acid, the active ingredient in vinegar. Acetic acid is a weak acid. As we have discussed, aqueous solutions of weak acids have increased concentrations of  $\text{H}_3\text{O}^+$  ions when compared to pure water. The following is the reaction of acetic acid and water:



The flavins in the cabbage react with excess  $\text{H}_3\text{O}^+$  ions and change color depending on how many are present. When the reaction is at equilibrium, the rate of the forward reaction equals the rate of the reverse reaction.

Mathematically, we can describe the rate of the forward reaction as follows:

$$\text{Rate}(\text{forward}) = k(\text{forward}) * [\text{CH}_3\text{COOH}][\text{H}_2\text{O}]$$

And this is the rate of the reverse reaction:

$$\text{Rate}(\text{reverse}) = k(\text{reverse}) * [\text{CH}_3\text{COO}^{-1}][\text{H}_3\text{O}^{+1}]$$

The square brackets refer to the concentrations of the species reported in units of mole/L.

When the system is in equilibrium, the pH stays constant, as does the concentration of the acetic acid molecules and the acetate anion. The water, however, has an interesting property. Pure water has a density of  $\sim 1.0 \text{ g/mL}$ . It varies slightly depending on temperature, but that is not enough to affect any chemistry occurring around room temperature. A sample of one mole of water occupies  $18.0 \text{ mL}$ , so the molarity of pure water is  $1 \text{ mol} / 0.018 \text{ L} = 55.5 \text{ mol/L}$ . Most of general chemistry is concerned with dilute solutions, where the concentrations are less than  $1 \text{ M}$ . Under these conditions, even if every acid molecule reacts with water, the concentration of the water is changed by less than 2 percent. Therefore, the concentration of the water in dilute aqueous solutions can be considered constant, independent of the progress of the reaction.

At equilibrium, then, where the rate of the forward reaction is equal to the rate of the reverse reaction, we get the following:

$$k(\text{forward}) * [\text{CH}_3\text{COOH}](55.5) = k(\text{reverse}) * [\text{CH}_3\text{COO}^{-1}][\text{H}_3\text{O}^{+1}]$$

If we move all the constants to one side, we get this:

$$\frac{k(\text{forward}) * 55.5}{k(\text{reverse})} = \frac{[\text{CH}_3\text{COO}^{-1}][\text{H}_3\text{O}^{+1}]}{[\text{CH}_3\text{COOH}]}$$

As long as we keep the temperature fixed, everything on the left is constant, and we give it a new name, called  $K_a$ , the equilibrium constant for a weak acid. It is easy to determine the  $K_a$  in lab. You prepare a known concentration of acetic acid in water. You measure the

pH using either the indicators we have discussed or a pH meter. The pH meter will give a more accurate and precise result. If we know the initial concentration of the acid and the pH of the equilibrium solution, we can use the balanced chemical equation to calculate the concentrations of all the species in the equilibrium mixture. If we plug the equilibrium concentrations in the equation above, we can calculate  $K_a$ . In a general chemistry class, you will be required to write an ICE table to clearly illustrate the stoichiometric relationships. The acronym ICE stands for initial, change, and equilibrium. The ICE table is just a formal way to organize the stoichiometric information to solve the problem.

In the case of acetic acid, if we prepare an initial solution that contains 0.100 M acetic acid, and we measure its pH, we find that the  $\text{pH} = 2.87$ . This pH can be inverted to give the concentration of  $[\text{H}_3\text{O}^+]$  at equilibrium:

$$-\log[\text{H}_3\text{O}^+] = 2.87 \rightarrow [\text{H}_3\text{O}^+] = 10^{-2.87} = 1.35 \times 10^{-3} \text{ M}$$

We know that there was already  $1.0 \times 10^{-7} \text{ M H}_3\text{O}^+$  in the pure water before the acid dissolved, but given the significant figures in our problem, we can ignore that in our calculation. If we form  $1.35 \times 10^{-3} \text{ M H}_3\text{O}^+$ , because the reaction stoichiometry is 1:1, we must have also formed  $1.35 \times 10^{-3} \text{ M CH}_3\text{COO}^-$ . The amount of reagent acid left is  $0.100 - 1.35 \times 10^{-3}$ . Again, to the correct significant figures, the concentration of the acetic acid at equilibrium is 0.099 M.

Therefore the  $K_a$  for acetic acid is  $(1.35 \times 10^{-3})^2 / 0.099 = 1.8 \times 10^{-5}$ .

What happens if we prepare an acetic acid solution that is twice as concentrated as this one? We can measure its pH and proceed as above. However, since we know the  $K_a$  of acetic acid, now we can also invert the procedure we used above and calculate the pH of the solution. We know the .200 M solution will have a lower pH than the 0.100 M solution. To calculate the pH, we again set up an ICE table. But this time we know the initial concentration of the acid and the acid equilibrium constant. In the ICE table we enter the initial concentration of the acid. We use a variable, usually “x,” to represent the amount of  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{COO}^-$  formed to reach equilibrium. To answer the question, we solve the math equation:

$$1.8 \times 10^{-5} = \frac{x^2}{.200 - x}$$

This is a quadratic equation that should be familiar from your algebra course. You can solve it using the formalism of quadratic equations, or you can make a simplifying assumption. We’ll try the simplifying assumption here. Since the  $K_a$  for acetic acid is much less than one, we know that the concentration of the dissociation products is much less than the concentration of the reagents at equilibrium. Mathematically, we can say that  $x \ll .200$ . Under these circumstances we can simplify the equation above.



$$1.8 \times 10^{-5} \cong \frac{x^2}{.200}$$

This is a perfect square and is easily solved.

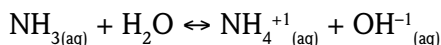
$$x^2 = (0.200 \times 1.8 \times 10^{-5}) = 3.6 \times 10^{-6}$$

$$x = (3.6 \times 10^{-6})^{1/2} = 1.9 \times 10^{-3}$$

This is the concentration of  $\text{H}_3\text{O}^+$ , so the pH of a 0.200 M solution of acetic acid is 2.72, lower than the pH of a 0.100 M solution, as we predicted.

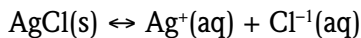
The acid equilibria for many acids have been measured and are tabulated in general chemistry books and a variety of reference texts.

There are fewer common weak bases than weak acids, but there are some. The most commonly encountered is ammonia  $\text{NH}_3$ . An aqueous solution of ammonia has a pH greater than 7 because of the following reaction:



The equilibrium is described in a manner exactly parallel to that of a weak acid, but this time the equilibrium constant gets a different subscript, a “b” to denote that the solution is basic. For ammonia solutions at 25°C, the  $K_b = 1.8 \times 10^{-5}$ . Ammonia is as strong a base as acetic acid is an acid.

It is worth noting a general principle here. The larger the numerical value of K, the larger the concentration of products at equilibrium. Just as the rate of chemical reactions spanned a huge range, the values of K for common chemical reactions range from almost zero to infinity. At the small end of the equilibrium constant range an example is the solubility of some essentially insoluble salts. The salts that precipitate in chemical reactions are considered “insoluble,” but it is rarely the case that all of the ions of interest precipitate out of an aqueous solution, even if stoichiometric amounts of ions are available. For instance, when we examined the precipitation of  $\text{AgCl}$ , we assumed all the silver ion was removed from the solution by the addition of chloride. But, in fact, the equilibrium expression for the dissolution of  $\text{AgCl}$  in water is as follows:



An interesting facet here is that in contrast to the aqueous components, the solid maintains a constant concentration as long as any of it exists. This is because the volume of the solid decreases as it dissolves. The concentration of the solid is therefore determined by its density, not the quantity of solid that is present in the two-phase mixture.

We can write the equilibrium expression for the dissociation as follows:

$$K_{\text{eq}} = \frac{[\text{Ag}^{+}][\text{Cl}^{-}]}{[\text{AgCl(s)}]}$$

Because this is an expression that includes both solids and aqueous solution, we need to be a bit thoughtful about calculating the numerical value. By recognizing that the  $[\text{AgCl(s)}]$  is constant, we can rearrange the equation to move all the constants on one side and rename it to make note of the change in its value.

$$K_{\text{sp}} = K_{\text{eq}}[\text{AgCl(s)}] = [\text{Ag}^+][\text{Cl}^-]$$

The value of  $K_{\text{sp}}$  for many “insoluble” salts is tabulated in chemistry texts and references. The  $K_{\text{sp}}$  for  $\text{AgCl}$  at  $25^\circ\text{C}$  is  $1.77 \times 10^{-10}$ . This means if you try to precipitate the silver ions from an aqueous solution, you will always leave some behind. On the other hand, soluble salts are always considered 100 percent dissociated in aqueous solution. The limit for them is based only on the solubility of the salt. The solubility constant for salt at room temperature is about thirty-eight. A saturated solution of  $\text{NaCl}$  contains 6.2 M  $\text{NaCl}$ . As long as you prepare a solution that is less than 6.2 M  $\text{NaCl}$ , you can assume all of the salt has dissolved and dissociated into ions. Of course, if you dissolve less salt, the system is not at chemical equilibrium.

It is always possible that salts dissolved in water will not simply separate into ions but may also undergo a chemical reaction called hydrolysis. When a salt that undergoes hydrolysis is dissolved in water, the pH can change significantly. Sodium chloride solutions have a neutral pH. But  $\text{NaF}$  solutions are slightly basic. What accounts for the difference?

If sodium ions were to react with water, they would form  $\text{NaOH}$ . We say that  $\text{Na}^+$  is the conjugate acid of  $\text{NaOH}$ . But we know that  $\text{NaOH}$  is a strong base, which stays 100 percent dissociated in water. So no  $\text{NaOH}$  forms when  $\text{Na}^+$  ions are present in water.

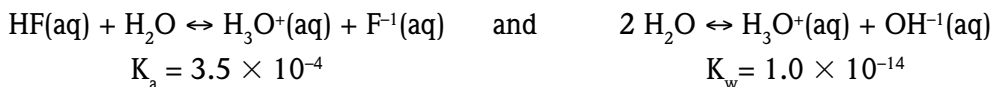
If chloride ions were to react with water, they would form  $\text{HCl(aq)}$ . We say that  $\text{Cl}^-$  is the conjugate base of hydrochloric acid. But  $\text{HCl}$  is a strong acid, which stays 100 percent dissociated in water. So no  $\text{HCl}$  forms when  $\text{Cl}^-$  ions are present in water.

But the situation is different when the anion is  $\text{F}^-$ . If fluoride ions react with water, they undergo the following reaction:

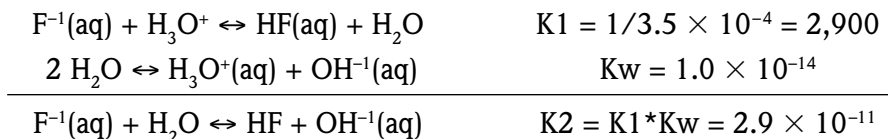


Since  $\text{HF}$  is a weak acid, with a  $K_{\text{a}}$  of  $3.5 \times 10^{-4}$ , some  $\text{HF}$  can form in aqueous solutions. If we revive some of the fun chemistry math we used in our discussion of reaction mechanisms, we can figure out the equilibrium constant for the reaction in which  $\text{F}^-$  undergoes hydrolysis.

The reactions we know:



If we reverse the HF equation and add it to the H<sub>2</sub>O equation, we get the following:

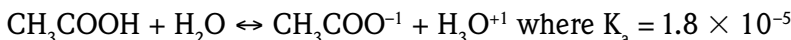


If we prepare a 0.10 M solution of NaF, it will dissolve completely to form 0.10 M Na<sup>+</sup> and 0.10 M F<sup>-1</sup>. The F<sup>-1</sup> will undergo hydrolysis:

$$\frac{x^2}{.10-x} = 2.9 \times 10^{-11} \text{ or } x^2 \cong (2.9 \times 10^{-11}) * 0.10$$

So  $x = (2.9 \times 10^{-12})^{1/2} = 1.7 \times 10^{-6}$ . Therefore, the concentration of OH<sup>-1</sup> in the solution of NaF is  $1.7 \times 10^{-6}$ . The pOH is  $-\log(1.7 \times 10^{-6}) \cong 5.8$ , and the pH = 14 - pOH = 8.2, which makes it slightly basic.

Solutions that contain reasonable quantities of both a weak acid and its conjugate base or a weak base and its conjugate acid (where the conjugates are usually produced by dissolution of a salt) have interesting and very important properties. Let's take the example of acetic acid and sodium acetate. If we place one-tenth mole of sodium acetate, a white solid, in a flask and dissolve it in a solution containing 0.10 M acetic acid, instead of water, the solution will rapidly come to equilibrium described by the following equation:

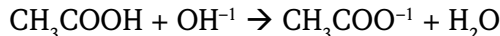


Doesn't look very interesting yet, does it? But let's remember that the solution contains an acid on the left as a reagent and an equivalent amount of its conjugate base on the right as a product. The first interesting thing is that this solution has a pH of 4.7. You will recall that the solution containing 0.10 M acetic acid had a pH of 2.87. We can explain the pH change using Le Chatelier's principle. When we add sodium acetate to the acetic acid solution, the equilibrium tries to use it up. In order to do that, it reacts to the acetate ion with excess H<sub>3</sub>O<sup>+</sup>, until an equilibrium condition is reestablished. The amount of H<sub>3</sub>O<sup>+</sup> present at this new equilibrium is considerably less than in the pure acetic acid solution, so the pH is higher.

But an even more interesting property is evident if we compare the behavior of this equilibrium system to that of a pure water equilibrium. Let's add 0.001 mole of NaOH(s) to two samples—the first is 100 mL of water, the second is 100 mL of this acetic acid/acetate solution.

In the water, the initial pH is 7.0. But after the NaOH dissolves, the OH<sup>-1</sup> concentration in the water is 0.001 mol/.100 L = 0.010 M. The pOH is 2.0 and the pH is 12. The addition of the NaOH changed the pH of the water by 5 pH units.

What happens in the acetic acid/acetate solution? The initial pH of the solution is 4.7. The  $\text{OH}^{-1}$  ions react with the strongest acid present—that's the acetic acid.



The strong base drives the reaction to completion, hence the one-way arrow. After the reaction the solution contains  $(0.010 - 0.001) = 0.009$  mole  $\text{CH}_3\text{COOH}$ , almost no  $\text{OH}^{-}$  because it all reacted, and  $(0.010 + 0.001) = 0.011$  mole of acetate anion. The pH is calculated from the following expression:

$$1.8 \times 10^{-5} = \frac{0.011 \text{ mol} / 0.100 \text{ L}}{0.009 \text{ mol} / 0.100 \text{ L}} * [\text{H}_3\text{O}^{+1}]$$

So  $[\text{H}_3\text{O}^{+}] = 1.47 \times 10^{-6}$ , or the  $\text{pH} = 5.83$ . Adding the same amount of  $\text{OH}^{-1}$  to the acetic acid/acetate ion solution only changes the pH by 1.1 units. This is much less of a change than the 5 pH unit change experienced by the water. The solution containing acetic acid and the acetate ion is called a buffer. It resists a change in pH. Buffers play a critical role in all biological systems and are also important in understanding many geological processes.

## For Greater Understanding

### Questions

1. Which of the following is true?
  - a. At chemical equilibrium all chemical reactions stop.
  - b. At chemical equilibrium the concentrations of the products and the concentrations of the reagents are equal.
  - c. At chemical equilibrium the rate of the forward reaction equals the rate of the reverse reaction.
  - d. At chemical equilibrium all the reagents have been converted to products.
2. A strong acid
  - a. is 100 percent dissociated in aqueous solutions.
  - b. always has a pH less than 1.
  - c. always has a  $K_a$  of 1.
  - d. is always at chemical equilibrium when dissolved in water.
3. Consider the following equilibrium constants. Assuming the stoichiometry of the reactions described is the same, which reaction would have the highest concentration of products at equilibrium?
  - a. The reaction with  $K = 10,000$ .
  - b. The reaction with  $K = 1$ .
  - c. The reaction with  $K = 0.1$ .
  - d. The reaction with  $K = 0.00001$ .

### Suggested Reading

American Chemical Society, and Jerry A. Bell. *Chemistry: A General Chemistry Project of the American Chemical Society*. New York: W.H. Freeman, 2005.

Pauling, Linus. *General Chemistry*. New York: Dover Publications, 1988 (1970).

### Other Books of Interest

Walker, Brian, and David Salt. *Resilience Thinking: Sustaining Ecosystems and People in a Changing World*. Washington, D.C.: Island Press, 2006.

## Lecture 12

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### Moving Electrons: An Introduction to Oxidation-Reduction

The Suggested Readings for this lecture are the American Chemical Society and Jerry A. Bell's *Chemistry: A General Chemistry Project of the American Chemical Society*, chapter 10: "Reduction-Oxidation: Electrochemistry," and Linus Pauling's *General Chemistry*.

The industrial revolution of the eighteenth and nineteenth centuries was supported by an increasing understanding of thermodynamics. Similarly, the electronic revolution of the late-twentieth century depended on our increasing understanding of how electrons can be liberated from or captured by materials through oxidation-reduction processes.

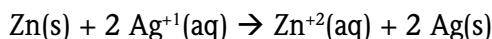
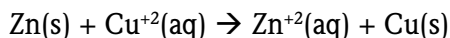
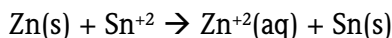
Almost all of chemistry involves moving electrons. An atom's position on the periodic table determines whether it is more likely to release electrons or accept them in a chemical process. Metal atoms with fewer than four valence electrons prefer to get rid of them, forming positively charged ions with full octets occupying their core electron shell. Nonmetals generally prefer to accept electrons, becoming negatively charged and gaining an octet of electrons in their valence shells. Transition metals follow a less obvious, but easily characterized, trend in behaviors. If we properly engineer the environment in which spontaneous chemical reactions occur, we can generate an electrical current and harness it to do work. Today, that engineered system is called a battery, but tomorrow technology may allow us to harness the power of fuel cells. Here we examine the chemistry behind both.

We can examine the relative tendency for metal atoms to give away their electrons by placing pure metal samples in solutions containing ions of other metals. If a reaction occurs, we say the metal in the sample is more active than the metal ions that are reduced in the reaction.

For example, let's put three pieces of copper foil in three different solutions. The first solution contains silver nitrate, the second zinc nitrate, and the third tin nitrate. Nothing happens in the zinc nitrate or tin nitrate solutions. But in the silver nitrate solution, it is almost immediately clear that a reaction is happening. A silver-colored coating appears on the copper, while the solution surrounding the solid turns light blue. The silver colored solid is, in fact, silver metal, and the blue color is from the presence of copper ions, which are released into the solution. We say that copper is more active than silver because the copper transfers two electrons per atom to two silver ions, reducing them to silver metal. The reaction is written  $\text{Cu(s)} + 2 \text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2 \text{Ag(s)}$ .

In this reaction the copper, which has given up electrons, is oxidized. The silver, which has accepted electrons, is reduced. It is easy to think of the "reduction" as referring to the decrease in the oxidation state of the metal ion from +1 to 0.

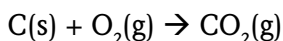
To verify the activity of this set of metals we can continue the experiment by adding solid pieces of zinc to separate samples of each solution and solid pieces of tin to samples of each solution as well. If we wait a while and examine the containers, we see that the zinc metal donates electrons to the silver ions, just like copper did. In addition, the zinc metal donates electrons to the copper ions in solution, reducing the blue color of the solution and producing a dark-colored solid. Zinc also donates electrons to the tin ions in solution, forming another dark solid that appears as the zinc metal appears to “dissolve.” Since zinc reacts with all of the metals in solution, we say that zinc is the most active of the four metals. Zinc is easily oxidized by tin, copper, and silver.



In each of these reactions, the zinc is oxidized, because its oxidation state increases from 0 to +2. The other metal is reduced. The zinc is called a reducing agent, because it facilitates the other metal’s reduction. The metal that is reduced is called an oxidizing agent. The reactions in which the more active metal is able to donate electrons to the less active metal are spontaneously moving electrons. If we can harness the moving electrons, we can use the spontaneous reactions to make a battery. The current that flows under the influence of the spontaneous chemical reaction can do electrical work.

Of course many chemical reactions, not just those involving metals, can be classified as oxidation-reduction processes. Two primary examples are combustion, source of the word “oxidation” for describing an increase in the oxidation state of an element when it chemically combines with oxygen in a reaction, and biological systems in that cascades of oxidation-reduction reactions are responsible for both the storage of energy in adenosine triphosphate (ATP, or cellular respiration) and the release of energy from ATP.

Let’s consider the combustion of coal (carbon) as a redox process.



First, we assign oxidation states to each atom in the reaction. Oxidation states allow us to keep track of the electrons and where they are going during the chemical reaction. Elements in their standard forms have oxidation states of zero. The oxidation state of a monatomic ion equals its charge. The sum of the oxidation states of the elements in a molecule is 0. The sum of the oxidation states on atoms in a polyatomic ion equals the charge on the ion. Metals have positive oxidation states when combined with nonmetals. The high electronegativity of oxygen and its valence means that it is always assigned an oxidation state of –2 when it is bound to other atoms. In the combustion of carbon, then, the oxidation states of both C and the oxygens in O<sub>2</sub> are zero. In the CO<sub>2</sub> product, the oxidation state of each O is –2, and therefore the oxidation state of the carbon is +4. We can view the reaction as happening when carbon atoms transfer four electrons, two to each

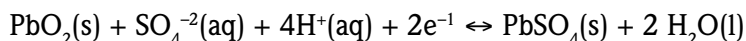
of two oxygens. The oxygen is reduced. The carbon is oxidized. It is generally true that an element to which oxygen is added in a reaction is oxidized.

A key biological oxidation-reduction process is the oxidation of glucose. The oxidizing agent is the oxidized form of nicotinamide adenine dinucleotide ( $\text{NAD}^+$ ). The species being oxidized, and therefore acting as the reducing agent, is glucose. The products are two pyruvate ions, two reduced-form  $\text{NADH}$ 's, four hydrogen ions, and energy. In biological systems, the energy is stored by coupling the  $\text{NAD}^+$  oxidation to the reaction, which produces two molecules of ATP from ADP's and phosphates.

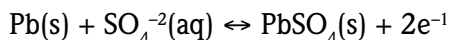
Harnessing the electron motion from spontaneous oxidation-reduction reactions requires physically separating the oxidation process from the reduction process. This is generally done by creating half cells. If we go back to our example of copper and silver, we could create two half cells by placing a piece of silver metal in a solution of silver nitrate in one container and a piece of copper metal in a solution of copper nitrate. The two pieces of metal are called electrodes. We could connect the electrodes using a wire with clips on the end. The clips would make good contact with the metals. For charges to actually move, however, we would need to complete the circuit. The connection to complete the circuit is commonly called a salt bridge. A salt bridge can be as simple as a strip of filter paper soaked in sodium nitrate solution so that it is wet and saturated with ions. The strip of filter paper can be draped between the beakers containing the solutions so that one end of the strip is in each solution.

As soon as the circuit is complete, the more active metal, copper, releases two electrons per atom. The electrons travel through the wire to the silver metal, where they attract the positively charged silver ions from the solution and reduce them to form silver metal that deposits on the surface of the silver electrode. As a result, the charge in the silver solution becomes less positive, and positive ions move through the salt bridge toward the silver solution, and negative nitrate ions move through the salt bridge toward the copper solution to reestablish the charge balance. The electrode that is releasing the electrons is called the anode. The electrode that is accepting the electrons is the cathode. Oxidation occurs at the anode and reduction occurs at the cathode in this spontaneous process. The electrons moving through the external wire can be harnessed to do electrical work, like energize a lightbulb or heat water. Commercial versions of this oxidation-reduction cell are called batteries.

A gasoline-powered car uses a lead-acid battery to start its engine. The reduction half cell is as follows:

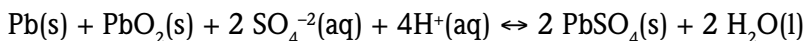


This is the oxidation half cell:





The battery in a car has a series of lead electrode grids suspended in a sulfuric acid solution. In a new battery, the alternating grids are filled with solid  $\text{PbSO}_4$  and mixtures of solid  $\text{PbO}_2$  and solid  $\text{PbSO}_4$ . When an external circuit is closed so that electrons can spontaneously move through the battery, the overall reaction that occurs is as follows:



The  $\text{Pb(s)}$  is oxidized to  $\text{Pb}^{+2}$ , and the lead in  $\text{PbO}_2$  is reduced from  $\text{Pb}^{+4}$  to  $\text{Pb}^{+2}$ . Once the car is running, the alternator provides current that runs this process in reverse by pushing the electrons in the opposite direction, thereby recharging the battery.

The battery does work on its surroundings in starting the car, and the alternator does work on the battery in recharging it. The work associated with a spontaneous redox process is calculated the same way that any electrical work is calculated: it is the amount of charge moved times the potential difference between the electrodes,  $w = C \cdot V$ .

The electrical potential for any half reaction is generally measured against an arbitrarily agreed-upon standard half cell. In the examples of metals and the lead-acid battery, the most common standard half cell is called the standard hydrogen electrode. A standard hydrogen electrode (SHE) consists of a platinum wire submersed in a 1.0 M solution of hydrochloric acid. When in operation, hydrogen gas at 1 bar (approximately 1 atmosphere) of pressure is bubbled around the platinum electrode, displacing the acid solution. The entire apparatus is maintained at 298°K. The reduction half reaction is  $2\text{H}^+\text{(aq)} + 2\text{e}^- \leftrightarrow \text{H}_2\text{(g)}$ . The potential of this half cell is defined to be zero as long as the standard conditions are maintained. To determine the potential of any other half reaction, we set up the SHE as one side of the system and the half cell of interest, using standard concentrations of 1M for any aqueous component, as the other side. The convention is to take the SHE as the anode in the cell. If the other half-reaction undergoes reduction and consumes the electrons produced at the SHE, the standard voltage is positive. If the other half reaction undergoes an oxidation, the standard voltage is negative.

In the example of biological redox reactions, however, a different zero is defined. Because biological systems are quite pH dependent, the standard state for biochemical half reactions is defined as occurring at pH 7 and at 37°C (body temperature). This biochemist's standard state is quite different from the chemist's standard state, 1M HCl at 298°K used in our discussions so far. The chemistry doesn't change because we change the standard state. The absolute numerical values we associate with particular half reactions do change, but the difference in potential between two half reactions is the same no matter which standard state we use. The term "potential" reminds us that the force that drives the electron motion depends on the difference between the two electrical environments and not on their absolute characteristics.

There are a wide variety of chemical systems that are used in commercial batteries. Recent innovations are improving lithium ion batteries. Lithium is the lightest metal on the periodic table. As electronic devices become lighter and smaller, the demand for small

but powerful batteries is becoming more intense. Automobile manufacturers also want the lightest possible batteries, and lithium ion technology will power the drivetrain of the first generation of commercially available all-electric vehicles.

Lithium ion batteries consist of lithium cobalt oxide,  $\text{LiCoO}_2$ , and carbon electrodes. The medium that allows the charges to move is the real technology focus in these batteries. Water has a high density and is therefore contraindicated if the goal is to make lightweight batteries. The charge carriers in lithium ion batteries are more commonly organic solvents or high-tech conductive polymers, which can be formed into thin films that carry charges quite efficiently.

The remarkable efficiency of biological systems has chemists investigating the possibility of mimicking biological systems by using glucose, oxygen, hydrogen, and some catalysts to build batteries that run without metal components.

Of course, as attractive as batteries are as an energy source, the direct conversion of solar energy into electrical energy is an even more attractive possibility. Direct conversion of solar radiation into either chemical or electrical energy provides the most sustainable form of electricity generation. The conversion of solar radiation into electricity is dependent on the properties of semiconductors. We have discussed the structure of metals, in which the atomic centers share their valence electrons in orbitals that are close together in energy space and extend throughout the entirety of the metal, allowing the electrons to migrate easily among the nuclear centers and conduct electricity when exposed to an external field. We have also discussed the structure of covalent molecules, where the electrons occupy localized molecular orbitals that are energetically separated from one another. Molecules may reorient in the presence of an external field, but they do not conduct electrical current unless the field is sufficient to ionize the molecules.

The elements on the periodic table that separate the metals from the nonmetals, which combine to form covalent molecules, have electronic structures that are intermediate between metallic and covalent. They include B, Si, Ge, As, Sb, Te, and Po. They are called semiconductors. The structure of semiconductors is intermediate between that of metals and that of covalent compounds. In semiconductors, the valence electrons occupy valence bands that are relatively localized on the atomic components. But the energy gap between the occupied and the unoccupied or conduction band is not so large as to prevent conductivity when appropriate amounts of energy are provided to lift some electrons from the valence into the conduction bands. The energy can be provided by high-temperature environments, or by direct excitation of electrons that absorb photons with sufficient energy.

It is also possible to affect the band gap, as the energy difference between the valence and conduction bands is called, by adding small quantities of impurities—atoms of another semiconductor, for instance. The most effective impurities added to semiconductors generally have occupied electronic energy levels that are just slightly lower in energy

than the conduction bands of the host or unoccupied levels just slightly higher in energy than the valence band of the majority component. Either of these structures reduces the band gap in semiconductors. The first material is called an n-type semiconductor, because negative electrons occupying the conduction band are primarily responsible for the system's response to an externally applied field. The second is called a p-type semiconductor, because electrical conduction is primarily associated with the motion of the positive "holes" left in the bulk when electrons move into the unoccupied levels.

When used as solar collectors, the advantage of semiconductors is that they efficiently convert the energy they absorb from solar radiation (photons) to electrical energy by exciting electrons in the semiconductor. The holy grail of solar energy production would be to harness the electrical potential produced to electrolyze water—that is, to split it into hydrogen and oxygen gas through a redox process. The subsequent combustion of the hydrogen and oxygen to reform water is highly exothermic and completely free of both carbon dioxide and the myriad side products that are the primary sources of pollution in today's petroleum-based society. Unfortunately, although semiconductors can produce sufficient numbers of electrons to make this conversion feasible, the energy required to promote the direct hydrolysis of water is high, too high for any known semiconductor to accomplish it directly. Some insightful chemistry has allowed the direct hydrolysis of water using a specific form of  $\text{SrTiO}_3$ , a semiconductor material whose use was motivated by the realization that titanium dioxide,  $\text{TiO}_2$ , the classic white stuff that lifeguards wear to protect their noses from sunburn, was spectacularly efficient at absorbing a wide spectrum



of solar radiation in both the visible and ultraviolet. But efficiencies are limited when the semiconductor only absorbs some of the solar radiation. Recent work has focused on two areas: the development of catalysts to reduce the voltage required to drive the hydrolysis reaction and the use of biological mimics of chlorophylls and related compounds that are responsible for harvesting solar energy in plants to increase the absorption spectrum of the solar collectors. So far, despite numerous advances, there is no economically competitive method for converting solar energy to hydrogen.

Another avenue of investigation for alternate energy production is the fuel cell. In fuel cells, a combustion reaction is conducted under conditions where its free energy is converted to electrical energy, and not to heat and light as is typical under the combustion conditions with which we are familiar. Because of the second law of thermodynamics, every time we convert energy from one form to another, we lose some to entropy. Therefore, the direct conversion of chemical energy to electricity maximizes the efficiency with which combustions can do electrical work. Hydrogen fuel cells have been developed and have been used extensively in space exploration and in specialty applications. The reaction is simply  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}$ . But today's fuel cells have two disadvantages—they need to operate at high temperatures and they are currently more expensive than other forms of electrical energy generation.

Research focusing on improving catalysts to allow lower temperature operations will help. Other research is focusing on the use of biological mimics as alternate fuels. For example, a glucose-oxygen fuel cell seeks to replicate the efficiency of glycolysis in aerobic organisms to convert the electrochemical gradient the process generates directly into electrical potential.

The technical advances that accompanied our increasing understanding of thermodynamics revolutionized Western culture in the nineteenth century. The rise of electronics in the twentieth century was no less impressive. There is every reason to believe that the twenty-first century could see the advent of technologies that will provide efficient, sustainable sources of electricity.

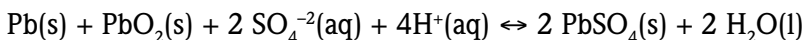
## For Greater Understanding

### Questions

1. The oxidized form of  $\text{Cu}^{+1}$  is

- a.  $\text{Cu(s)}$       b.  $\text{Cu}^{+2}$       c.  $\text{e}^{-1}$       d.  $\text{O}^{-2}$

2. Identify the oxidizing agent in the following reaction:



- a.  $\text{Pb(s)}$       b.  $\text{PbO}_2\text{(s)}$       c.  $\text{SO}_4^{-2}$       d.  $4\text{H}^+$

3. Among the advantages of fuel cells is that

- a. they are cheap.  
b. they are efficient.  
c. they are small and lightweight.  
d. they only produce hydrogen.

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### Other Books of Interest

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## Lecture 13

### Environmental Chemistry

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The Suggested Readings for this lecture are Colin Baird and Michael Cann's *Environmental Chemistry* and Rachel Carson's *Silent Spring*.

Pollution is an ugly word, one that we usually associate with the by-products of our industrial age. In fact, history clearly shows that society's expectation that our world is infinitely large and can dilute the effects of any toxin we deposit in it, from feces to nitric oxide, is badly mistaken. Both water and air pollution are serious concerns in every populated part of the world today. The optimist notes that this pollution arises in exchange for higher agricultural productivity, improved medical care, and generally longer lives, lived more comfortably than any previous generation. In this lesson we will discuss some types of air and water pollution, how pollution levels are measured, and what today's realist chemists are doing to try to rectify the mistakes of the past and further improve living conditions in the twenty-first century.

The modern era of pollution management owes its beginning largely to one woman—Rachel Carson. In her 1962 book *Silent Spring*, Carson highlighted the environmental cost of using DDT (dichlorodiphenyltrichloroethane), an effective pesticide against both fire ants and mosquitoes. Although it is only moderately toxic, DDT is of specific concern because it and its primary degradation products, DDE (dichlorodiphenyldichloroethylene) and DDD (dichlorodiphenyldichloroethane) are fat soluble and bioaccumulate. DDT is known to disrupt normal endocrine activity in humans and is categorized as a “probable” carcinogen by the U.S. Environmental Protection Agency. Carson highlighted its effects on birds, where it was implicated in eggshell thinning, which led to a decline in the birth rate of several birds of prey, including the American national symbol, the bald eagle.

Carson's efforts allow us to define “pollution.” Pollution, ultimately, is simply a biological or chemical compound in a location, or in a quantity, where it is either hazardous, or not wanted. DDT is still in use in specific locations around the world where the risks of malaria and other mosquito-borne diseases are perceived as higher than the risks of using DDT. But even the most aggressive use of DDT today eschews the wholesale spraying seen during World War Two and through the 1950s, where the attitude seemed to be “if a little is good, more is better.” Today's applications are targeted and use a minimal amount of material to optimize the effectiveness of the pesticide while minimizing its side effects.

There are some chemical compounds like DDT that are particularly toxic to life and therefore are always of concern. The vast majority of pollutants, however, can be perceived of as paralleling apple peels in the process of making an apple pie. If you don't manage the apple peels properly, they will rot and ferment over time and may release an odor you would consider offensive, or attract bugs and critters you do not want in your kitchen. But

a gardener would be happy to take those apple peels from you and place them in a compost pile. For a fastidious cook, the peels are waste and could be viewed as polluting the kitchen environment. But to the gardener, they are a useful commodity. Historically, we just haven't been very attentive to managing and finding use for the waste from chemical processes, but more and more attention is being paid to this issue.

Let's consider water pollution first. Our existing water standards are defined in terms of the concentrations of hazardous materials in natural water, rain, groundwater, and drinking water. The standards are established in response to human health concerns, our ability to detect and quantify the biological and chemical species of interest, and our increasingly sophisticated understanding of how biological and chemical systems modify chemicals over time. We won't dwell on the biological here. Suffice it to say that Mother Nature is often cruel. Natural bodies of water and shallow wells are typically host to a wide variety of microorganisms, some of which pose a hazard to human health, some of which do not. But the human history of water-borne illnesses certainly predates the modern era. Today we manage most water-borne biohazards by killing them, or separating them from the water. This is a generally centralized process in the West, and it is becoming a more centralized process in the third world as it develops.

Geological features in contact with natural waters can contaminate those waters with chemical species we categorize as pollutants. Radon (Rn), a noble, radioactive gas, is produced by the decay of uranium occurring naturally in many soils. Radon can dissolve in groundwater and poses a risk to human health. Nitrates, a variety of heavy metals and high levels of fluorides, pose specific natural risks to groundwater supplies in some geographical regions of the United States. Though not usually considered a pollutant, some areas have hard water, which has a high concentration of magnesium and calcium ions. Hard water produces scale, a nuisance for maintaining plumbing fixtures and in cleaning.

Of course, the sum of human activity causes most water pollution. Historically, water quality in the United States was an issue as early as the 1880s. Ellen Swallow Richards, the first woman to earn a chemistry degree in the United States, served the Commonwealth of Massachusetts as its official water analyst from 1887 until 1897. In 1887, she managed the first study of water quality in United States history. After the study, which indicated elevated chloride levels in many water sources, Massachusetts built the first modern sewage-treatment plant.

Today, there are more sources of water pollution than in the 1880s. Large oil spills in natural waters cause immediate damage to ecosystems and wildlife, can threaten human health, and require extensive remediation. Fertilizer and pesticide runoff from agriculture and household use is a major source of surface- and well-water pollution. Inappropriate handling of human wastes is probably the oldest source of water pollution. Manufacturing and mining can release heavy metals, organic pollutants, and excessive heat, all of which can adversely affect water quality. The increasing presence of legal pharmaceuticals in public drinking water supplies is becoming a more acute issue. Old pills get flushed for

disposal or simply pass unaffected through the body and are excreted by the patient.

Public water systems and home wells can be configured to mitigate all these pollutants and remove them from water, or reduce their concentrations to acceptable levels. We'll consider metals in detail. Since metals are hazardous when present as dissolved ions (not in the metallic form), they can generally be removed from water by ion exchange, sequestration, or precipitation. Many popular water filters use physical filtration, not too different from a coffee filter, to separate sediments (essentially anything present in a large enough particle) from drinking water. Ion exchange resins are an example of better living through modern chemistry. Resins are composed of organic polymers with ionizable functional groups attached. For instance,  $\text{-SO}_3\text{H}$  acts as a strongly acidic functional group in some resins. Its  $\text{H}^+$  ion is highly labile and is easily exchanged with metal ions when they are available. Multiple charged metal ions (like lead) need to be able to bind to two sites simultaneously, so that the overall neutral charge of the resin is maintained. This dictates the separation of functional groups required to make an effective resin. While leaving the water "cleaner" the resin obviously becomes "polluted" following the exchange. In the ideal scenario, we would remove the pollutants and deliver them to an application in which they were useful and nonhazardous, while restoring the resin to its initial condition so it could be used again. Some resins can be repeatedly regenerated, but, of course, we do not live in an ideal world.

Water filters also use activated charcoal, or zeolites, to trap metal ions and sequester them from drinking water. Both activated charcoal and zeolites can be thought of as three-dimensional mazes. The water flows through, but charged species, like metal ions, get trapped in specific locations where they are surrounded by ions of opposite charges. Both natural and synthetic zeolites are known. In the synthetic versions, much effort goes in to producing zeolites with specific charge and size characteristics so the capture zones in the maze can be customized to remove specific pollutants.

Modern water softeners use zeolites that trap calcium and magnesium, and release sodium ions in an exchange process. A salt brine reservoir can be used to recharge the softener, releasing the calcium and magnesium and replacing them with sodium. While soft water prevents scale deposits on plumbing fixtures and improves the action of soaps, the high sodium concentration in soft water can be detrimental to the health of those who need to minimize their sodium intake. High sodium concentrations can also damage plants, which utilize the magnesium and calcium, and can raise the salinity level of wastewater streams. Facilities that soften water may solve a local problem but contribute to a larger problem downstream.

A variety of anions can be added to water to precipitate metal pollutants, removing





them from the water supply by forming essentially insoluble compounds. Ellen Swallow Richards reversed this process, using silver ions to precipitate chloride from the water samples she collected in Massachusetts, when she realized that excessive chloride was correlated with polluted water.

Unfortunately, Mother Nature's chemistry is less absolute than we might like. Even "essentially insoluble" salts leave some ions in solution when they form an equilibrium mixture. Consider lead, a pollutant and neurotoxin. Bioactive lead ions might be removed from water by precipitating them with chloride ions. The  $\text{PbCl}_2$  will precipitate until the product of the concentration of remaining chloride,  $\text{Cl}^-$ , in moles per liter, multiplied times itself and then times the concentration of the remaining lead +2 ions in moles/liter, equals  $1.7 \times 10^{-5}$ . Chemists say that the solubility product of  $\text{PbCl}_2$  is  $1.7 \times 10^{-5}$ . This sounds like a small number, doesn't it? And it is. But is it small enough?

As of 2011, the U.S. Environmental Protection Agency has set zero as the concentration of lead that causes no known health risks, and 0.015 mg/L as the "Maximum contaminant level" allowed in drinking water. When converted to moles, 0.015 mg Pb/L becomes the following:

$$0.015 \text{ mg} \times (1.0 \text{ g}/1,000 \text{ mg}) \times (1 \text{ mole Pb}/207.19 \text{ g Pb}) = 7.2 \times 10^{-8} \text{ mole/L}$$

The solubility of NaCl at room temperature is much greater than 1 mole/L, so if we mixed 1 mole of NaCl (solid) in 1 L of water containing the legal limit of 0.15 mg/L lead, and assume that the volume does not change, the product of the lead concentration times the chloride concentration squared (because there are two Cl's for every Pb) would be  $1 \times 7.2 \times 10^{-8} \text{ mol/L} = 7.2 \times 10^{-8}$ . This product is much smaller than the solubility product for  $\text{PbCl}_2$ , so no solid  $\text{PbCl}_2$  precipitate forms, and both the lead ions and chloride ions stay in the water. To remove lead from our drinking water, we need an ion that has a smaller solubility product. One simple choice is PbS. The solubility product of lead sulfide is  $3 \times 10^{-28}$ . Therefore, by adding NaS to the water sample, we will form solid PbS, which will fall to the bottom of the container holding the solution. The concentration of lead left behind in the water will be less than the square root of  $3 \times 10^{-28}$ , less than  $1.7 \times 10^{-14}$  mole Pb/L. This is not zero, but converted to mg/L, it is  $3.5 \times 10^{-9}$  mg/L, well below the action level and a big improvement.

Unfortunately, in this example, we have used a huge excess of  $\text{Na}_2\text{S}$ . The excess allows us to minimize the amount of lead left in the water, but it leaves a lot of sodium and sulfide ions behind. We already know that sodium ions can be of concern. What about sulfide? Most natural waters are slightly acidic. The extra sulfide ions can combine with excess  $\text{H}^+$  ions and form  $\text{H}_2\text{S}$  gas. The gas will bubble out of the water over time, like  $\text{CO}_2$  gas bubbles out of a carbonated drink. Unfortunately, the  $\text{H}_2\text{S}$  is the chemical associated with the odor of rotten eggs. In using the sulfide to remove the lead, we are producing water that smells like rotten eggs. In chemistry, it really does seem like sometimes you can't win.

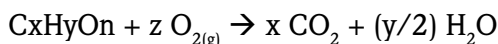
The preceding discussion does not present a realistic nor comprehensive view of

water treatment today. But it does highlight some of the complications that fundamental chemistry places in the way of our efforts to provide clean water for everyone on Earth. And it highlights how solving one problem can lead to others.

Air pollution is often perceived of as a problem localized to cities and specific industrial sites. But long-term studies of the migration of pollutants through the atmosphere and recent discussions of global warming emphasize that our atmosphere does not represent an infinitely large depository for our gaseous wastes any more than our rivers and oceans do.

The most important source of air pollution for most people is cigarettes. Cigarette smoke contains a number of hazardous chemicals. The easiest way to clean your local air supply is to stop smoking.

However, there is no question that our hydrocarbon-dependent era is increasing the concentration of carbon dioxide and other pollutants in the atmosphere. Of course, plants need carbon dioxide in the same way we need oxygen. So plants might actually be benefitting from higher carbon dioxide levels. And ironically, from a chemical standpoint, carbon dioxide is the *best* product that hydrocarbon combustion produces. Chemists describe the complete combustion of hydrocarbons and oxygenated hydrocarbons, including gasoline, fuel oil, wood, natural gas, and alcohol, by an equation of this form:



This is described as the complete combustion of the fuel because all of the carbon in the fuel is converted to carbon dioxide. The oxidation state of the carbon in the fuel is always  $-4$  or  $-3$ , whereas in  $\text{CO}_2$  the oxidation state of carbon is  $+4$ . Four is the most positive oxidation state that carbon has under any accessible conditions. On the other hand, if we try to reduce the carbon dioxide concentration by only partially combusting the fuel, carbon soot (oxidation state zero) or carbon monoxide is produced. Carbon soot and carbon monoxide are chemical pollutants because of their ability to participate in further reactions in the atmosphere and within the human body. Carbon monoxide is actually acutely toxic to humans because of the ease with which it mimics oxygen in interactions with hemoglobin. But  $\text{CO}_2$  is the compound of concern when the topic is global warming. Any chemist will tell you, however, that as long as carbon containing fuels are burned,  $\text{CO}_2$  is the chemical product of choice.

Other hazards of combustion are nitrogen oxides,  $\text{NO}_x$  compounds, which are formed partially by nitrogen contaminants in coal and oil, and partially in the high-temperature environments associated with combustion when air, which is  $\sim 80$  percent nitrogen, is used as the source of oxygen. Coal is specifically cited as the major contributor of sulfur oxides to atmospheric pollution, because sulfur is present as a contaminant in most coal. To make matters worse, both nitrogen oxides and sulfur oxides react with water in the atmosphere and contribute to acid rain, polluting surface waters.

In a pure oxygen environment, where the fuel is free of nitrogen contamination, the combustion of a hydrocarbon would not produce nitric oxides, because no nitrogen would

be present. If coal were free of trace sulfur, the combustion of coal would not produce sulfur oxides. In today's cars and industrial applications, modern technology is helping to reduce the emission of these two pollutants.

Your car's catalytic converter does three things for the environment. It uses sophisticated catalysts to complete any oxidations that did not happen in the engine itself, converting any CO to CO<sub>2</sub>; and any -CH-containing compounds that pass through it to CO<sub>2</sub> and water. At the same time, it reduces the NO<sub>x</sub> produced in your engine to diatomic nitrogen gas.

All NO<sub>x</sub> is considered a serious air pollutant because it reacts with volatile organic compounds in the atmosphere and, when initiated by ultraviolet light in sunlight, forms ozone. While stratospheric level ozone is essential to life on the planet, ground-level ozone causes health issues, especially affecting the lungs in susceptible individuals. Ozone warnings are a common occurrence in many cities around the world, especially in the summer, when the solar radiation is more intense.

Industrial combustion emissions are highly regulated in the United States. A wide variety of pollutants can be reduced substantially by careful control of combustion conditions and the installation of "scrubbers" installed in exhaust lines. Scrubbers can remove soot, heavy metal trace contaminants, NO<sub>x</sub>, and SO<sub>x</sub> from any fuels in a variety of industrial settings. The technology ranges from straightforward filtration to the use of a variety of liquid sprays that contain compounds that attract and react with pollutants either electrostatically or by taking advantage of their acid/base properties.

Concern about global CO<sub>2</sub> levels has led to newer technologies that sequester the carbon dioxide produced by industrial furnaces. Some approaches convert the CO<sub>2</sub> into sodium bicarbonate. But the holy grail would be to directly convert the CO<sub>2</sub> to a commercially useful material. A test plant in California is evaluating the technical and fiscal feasibility of sequestering CO<sub>2</sub> and using other waste materials to form cement. In the spring of 2011, students at Michigan Technological University demonstrated a new CO<sub>2</sub> scrubber that converts waste CO<sub>2</sub> into "a building material." If either of these approaches can be scaled up economically, we have the ideal scenario of producing a valuable product from waste material.

It took less than one hundred years for us to go from the first comprehensive test of water quality to the establishment of the EPA, the realization that pollution control was essential to ensure the public good, and the implementation of a variety of technologies that allow us to enjoy cleaner water and air, despite the high levels of energy and goods we consume every day.



A scrubber on the smokestack of a coal-fired electricity-generating plant.

## For Greater Understanding

### Questions

1. Pollution
  - a. did not exist before the industrial revolution.
  - b. is getting worse as the world's population increases.
  - c. can be reduced over time by the use of technology.
  - d. is due exclusively to modern industry.
2. Lead can be removed from water
  - a. completely by precipitation.
  - b. to below the EPA's "maximum contaminant level" by precipitation.
  - c. because it is a metal.
  - d. completely by ion exchange.
3. Carbon dioxide
  - a. is a fuel.
  - b. is the worst possible product of coal combustion.
  - c. is the preferred product of coal combustion.
  - d. is only produced by automobiles burning gasoline.

### Suggested Reading

Baird, Colin, and Michael Cann. *Environmental Chemistry*. 4th ed. New York: W.H. Freeman, 2008.

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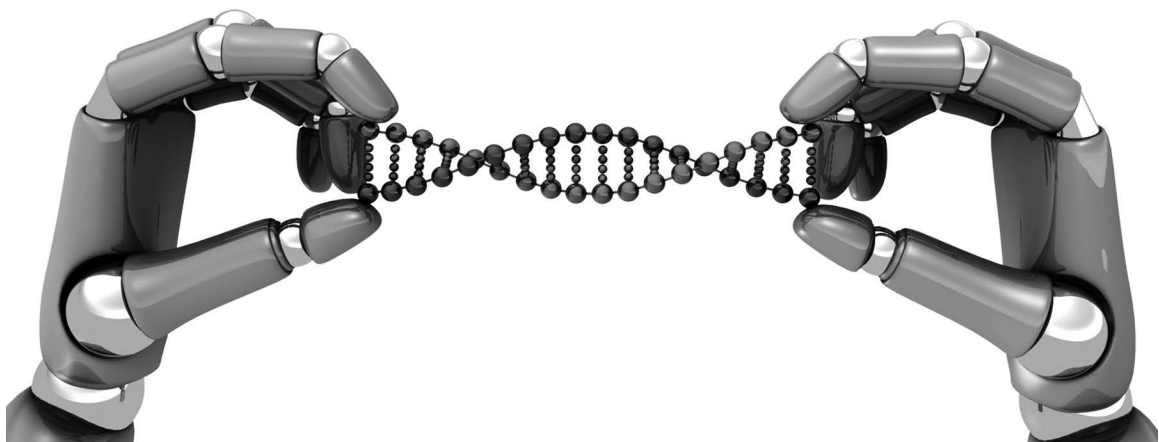
## Lecture 14

### Chemistry in the Twenty-First Century

The Suggested Readings for this lecture are *The New Chemistry*, edited by Nina Hall, and Mark A. Ratner and Daniel Ratner's *Nanotechnology: A Gentle Introduction to the Next Big Idea*.

Chemists in the twenty-first century are working to overcome the mistakes of the past and create a clean, healthy energy- and resource-efficient tomorrow. The chemical industry now recognizes that waste is a cost to manufacturers and consumers, not a benefit to corporations. Nanoscale devices promise improved functionality while demanding less in the way of raw materials and promising lower energy consumption. Recognition that we have only limited quantities of petroleum is forcing chemists to search for alternative, renewable sources of starting materials for a wide variety of products from fibers to pharmaceuticals. Energy efficiency is mandated, not an option. Improved separation and detection methods are pushing the limits of our ability to measure contaminant concentrations to sensitivities that were unimaginable even fifty years ago. And our understanding of spectroscopy and ability to build highly sensitive instrumentation and communicate with it, even from the depths of space, promise a future of discoveries we cannot yet imagine.

In fact, chemistry at the beginning of the twenty-first century would be almost unrecognizable to a chemist from the dawn of the twentieth century. The periodic table has expanded dramatically, adding more than thirty-one elements. Many of them are radioactive with short half-lives and exist only in reactors. But it is possible that in the near future we will be able to determine whether the predicted “island of stability,” which may be centered on nuclei with 120 or 126 protons, actually exists. If so, heavy atoms may be technologically useful in the next century.



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In the twentieth century, the quantum revolution completely overturned our understanding of atomic and molecular structure. Along with the development of the computer, quantum mechanics has allowed spectacular refinement in virtually every branch of chemistry. It is possible to calculate the structure and properties of both stable chemical species and exotic species found only in the most extreme environments. Spectroscopy allows direct and spectacularly detailed investigations of atomic and molecular structures. The structures of naturally occurring materials have been discerned, and many can now be synthesized in the lab by reaction methods and polymerization techniques unknown a century ago. It is feasible to determine the concentrations of almost any species in almost any environment. The time resolution with which chemical reactions can be glimpsed dropped in 2011 from the femtosecond ( $10^{-15}$  seconds) regime to the attosecond ( $10^{-18}$  seconds) regime. Whereas at the beginning of the twentieth century chemical reactions could only be discussed in terms of reagents and products, today reactions can be watched as they unfold, and even the most unstable intermediate can be followed over its brief lifetime.

One significant movement influencing the chemical enterprise in the twenty-first century is “green chemistry.” Green chemistry dates officially from the establishment of the Green Chemistry Program at the U.S. Environmental Protection Agency in the 1990s, although rumblings of it can be found in academic and government labs at earlier dates. The goal of green chemistry is to reform the practice of chemistry to prevent pollution. To accomplish this goal, practitioners of green chemistry subscribe to a number of basic principles, including using sustainable raw materials, designing and conducting synthesis to avoid generating hazardous by-products that require waste disposal, substituting less hazardous and less toxic chemicals in chemical reactions or lab tests, performing academic lab activities on a small-scale or micro-scale level to reduce the amount of chemicals used, and using catalysts to avoid by-product formation in chemical reactions and to reduce the need for high-temperature or high-pressure conditions for chemical reactions.

Ultimately, the goal of green chemistry is to realize “atom economy” using renewable raw materials and minimizing the use of toxic components. In a 100 percent efficient chemical process, every atom consumed is converted to desirable products with no waste produced. Green chemistry is helping to reframe the *zeitgeist* of the chemical industry from one in which waste is something to be disposed of to one in which waste represents a cost to industry, as it represents starting materials that are paid for, but not converted to valuable products. This description of waste as something having a negative impact on the economic bottom line means that atom economy is not simply good environmental practice, but good business practice as well.

One area of substantial concern in green chemistry is finding replacements for volatile organic solvents. Volatile organic solvents are molecules that have relatively low boiling points, and therefore high vapor pressures. Some familiar solvents might include formaldehyde, gasoline, ethyl acetate, or acetone. Although not acutely toxic, they have

been implicated in the formation of atmospheric pollutants and some are suspected of having negative health effects with long-term exposure. It is important to note that volatile organic compounds are not simply manmade; there are substantial natural sources of volatile organic compounds as well. When you walk in the woods, you are exposed to methane from rotting biomass and the good smell of isoprene and a variety of terpenes that are produced by plants as they grow. Chemists value organic solvents because they are less polar than water and therefore vary in their ability to dissolve a variety of materials. They also have different electronic properties from water and provide electronic environments that chemists can exploit to promote specific chemical reactions.

The most valuable substitute for volatile organic solvents is a class of materials called ionic liquids. These are just what they sound like—ionic materials that are liquids near room temperature. Most ionic liquids have either an anion or cation that is large compared to a typical inorganic salt. The first room-temperature ionic liquid (an “amine”:  $[\text{CH}_3\text{-CH}_2\text{-NH}_3^+][\text{NO}_3^-]$ ) was discovered in the early twentieth century and has a melting point of  $12^\circ\text{C}$ , so it is a liquid at room temperature. More recently, interest in binary ionic liquids has developed. Binary ionic liquids contain two different salts and have properties that vary systematically with the relative concentrations of the components. A well-studied binary system is 1-ethyl-3-methylimidazolium chloride ( $[\text{emim}]\text{Cl}$ ) mixed with  $\text{AlCl}_3$ . Despite its terrifying name  $[\text{emim}]\text{Cl-AlCl}_3$  mixtures are very effective solvents, dissolving substances including  $\text{C}_{60}$  and a number of polymers that resist forming solutions with molecular organic solvents. They are “green” because of their low vapor pressures, and because it is possible to tune their physical properties and electronic environments by varying the concentrations of the two components. The solution environment in ionic liquids is so different from that of water or volatile organic solvents that the basic rules of thermodynamics and reaction kinetics developed by studies of molecular solvent environments need to be reimaged. Ionic liquids provide a unique environment to the extent that an entirely new chemistry is being developed to exploit their characteristics.

Although in current manufacturing it is far from green, nanotechnology promises an alternate arena in which new chemistries will develop. At the nanoscale, the physical, chemical, and electronic properties of materials are often as extraordinarily different from those at the macroscale as ionic liquids are different from molecular solvents. This is because nano behavior is controlled by quantum mechanics to an extent not realized in

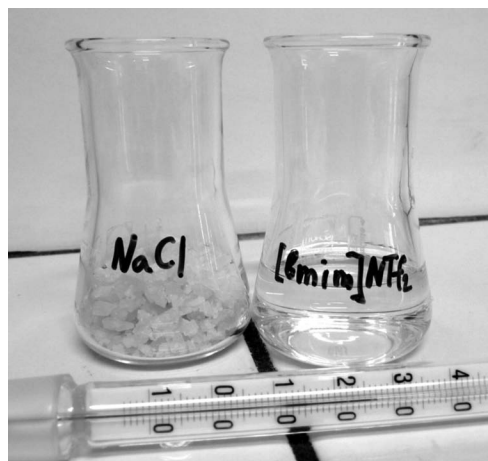
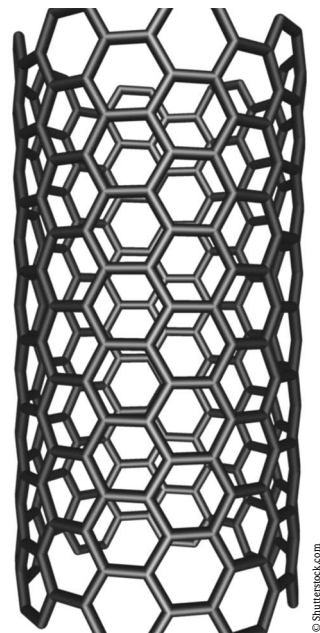


Table salt  $\text{NaCl}$  (left) and 1-butyl-3-methylimidazolium-based ionic liquid  $[\text{bmim}]\text{NTf}_2$  at  $27^\circ\text{C}$ .

other systems. Nanotechnology, the art and science of building devices that are 1 to 100 nanometers in dimension, is still in its infancy. The discovery of fullerenes, closed forms of pure carbon,  $C_{60}$  and  $C_{70}$ , now known to be ubiquitous in common soot, has ushered in an era in which pure carbon has the potential to play a more substantial role in technology. Nanoscale tubes made of carbon are extraordinarily strong. In much the same way that three-dimensional carbon structures form diamonds, among the hardest materials known, tubes of carbon atoms of the correct, small diameters can form incredibly strong fibers. The fibers will be strong enough that cables made by intertwining them are expected to support space elevators that will carry goods and people into space at a fraction of the costs of current rocket-based transport. This strength is a unique consequence of the covalent network that binds carbon atoms together when they form nanotubes.

The continuous decrease in size and power consumption, accompanied by the increase in speed of computer chips, is one of the most obvious benefits of the transistor's approach to the nanoscale. The development of smaller, faster computer chips is an example of technological innovation reducing the demand for raw materials. Nanoscale silicon devices will also reduce the demand for energy on a per operation basis, but the increasing number of operations per unit of material may prevent that economy from being realized to any appreciable extent. Solid-state nanoscale memories for computers could allow storage of information using entirely new protocols and at unimagined densities by exchanging electrical charge for light photons or quantum state as the means of storage.

Molecules are nanoscale devices, too. Clever design of molecular components can allow individual molecules to store information as well. Photochromism is the property a material exhibits when it changes color when exposed to light. The color change is due to a physical rearrangement of the atoms in the molecule. The most valuable photochromic molecules absorb a different color of light once they have converted to the second physical configuration. This allows one to "write" information with the first color of light and "read" it with the second. Of course, both physical states of the photochromic molecule must be stable in the long term to create a useful information storage device. An important class of photochromic materials is fulgides. Fulgides are ring compounds that contain a five-membered ring with one oxygen atom covalently bonded to form a ring with four carbon atoms. The two carbon atoms on either side of the oxygen are double bonded to other oxygen atoms, while the remaining two carbon atoms can have a variety of substituents attached to them. The substituents on the ring control the color, energetics, stability, and dynamics of the two forms of the molecules. Chemists are examining a wide variety of



A three-dimensional rendering of a carbon nanotube.

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substituents with the goal of producing stable storage devices for information, among a variety of other applications. You may not consider your photochromic sunglasses to be information storage devices, but they, too, work because of the unique properties of fulgides.

Equally impressive and revolutionary are chemistry's sophisticated mathematical tools that allow implementation of quantum mechanics and statistical mechanics to model everything from the energy states of atoms and the structure of molecules, to the design of pharmaceuticals, models of their avenues of action, and predictions of their effectiveness and side effects. In the same way that one can mathematically describe a circle from a geometrical perspective as the set of points in a plane that are a fixed distance from a given point, or from an algebraic perspective as the set of  $x, y$  coordinates that satisfy the equation  $x^2 + y^2 = c$ , clever mathematicians and chemists have redefined the unsolvable equations of quantum mechanics, morphing them into equations that can be solved iteratively to an arbitrary degree of precision. As computers become more powerful, the accessible options for redefinition are becoming broader and the limits of precision in determining solutions are becoming smaller. Modern computational methods allow us to calculate the energy of electron arrangements in atoms to higher precision than we can measure, to predict the structure of new chemical species and to predict their reactivities, and to examine the statistical behavior of the huge quantities of molecules found in even the smallest observable samples. As computers are made smaller and faster, and more sophisticated mathematical approaches are developed, questions that once took years to answer can now be investigated overnight on a researcher's desktop.

Even the complexities of biological systems are yielding their secrets to molecular modeling. The structures and dynamics of the lipid bilayers important in cell structure can be investigated using a mathematical method called "molecular dynamics." Labile systems that have resisted direct experimental observation reveal their secrets under the microscope of molecular dynamics. The effects due to the presence of unsaturated components like cholesterol in bilayers are clearly demonstrated by these computational methods. As the ratio of unsaturated components increases, the bilayer becomes more rigid and can produce a phase change where highly aligned parts of the layer appear to behave like ice cubes floating on the surface of water. This phase behavior may play a critical role in protein assembly and cellular and intercellular communication.

Modern chemistry is also making progress in supporting the development of alternative fuels. Today, less than 5 percent of the world's energy comes from alternative sources like solar, wind, and geothermal. Chemical advances have supported increased efficiencies in these areas; however, most experts agree that they will never be able to meet society's energy needs in the future. The only viable chemical strategy for alternative energy seems to lie in hydrogen. Hydrogen can be used in combustion processes to produce heat or in fuel cells to produce electricity. Hydrogen has two great advantages: it contains a lot of chemical energy for its mass, and the by-product of its use as a fuel either electrochemically or via combustion is water. So why isn't hydrogen already in use? The problem is mostly

economics. Like all good fuels, including gasoline and natural gas, hydrogen is explosive under certain conditions. But just as engineering manages the explosive hazards of today's fuels, it will manage the hazards of hydrogen in the future. The economic cost is in generating the hydrogen. In much the same way as we currently drill for oil and natural gas, or mine coal, we need to do work to get hydrogen.

Today, most hydrogen is produced by steam reforming, in which steam is reacted with natural gas:  $2 \text{H}_2\text{O}(\text{g}) + \text{CH}_4(\text{g}) \rightarrow 4 \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$ .

In the long term, this process has several disadvantages. First, the high heat capacity of water means that it takes a lot of energy to form the steam. Second, it requires natural gas, and third, it produces  $\text{CO}_2$ , the molecule most responsible for global warming. Clever design of catalysts can reduce the amount of energy that must be provided for this reaction. In the short run, the process can become greener by designing high efficiency solar boilers to directly heat the water. But it would be even better to design solar-powered photovoltaics that could accumulate solar energy and use it to split water into hydrogen and oxygen electrochemically. Electrochemical processes are theoretically quite efficient, and a substantial amount of progress has been made in recent years on designing new semiconductor and nano-featured materials to increase the efficiency of hydrogen production using solar energy. It would be greener still if we substituted a renewable source of carbon for the methane. A variety of agricultural and waste materials from farming have been examined as suitable sources of carbon, including peanut shells, grease, and plastics. Each feedstock requires its own set of catalysts and its own set of scrubbers, as each presents a unique profile of potential pollutants.

Ultimately, we would use the hydrogen to generate electricity in a fuel cell. This direct conversion to electricity is more efficient than burning the hydrogen and producing electricity using a traditional generator. A fuel cell is similar to a battery in that it harnesses spontaneous reactions in an environment where oxidation-reduction processes are favored. But a fuel cell differs from a battery in that it is an open system into which hydrogen and oxygen are continuously fed. In the fuel cell, the hydrogen first passes over a catalyst that splits the hydrogen molecule into protons and electrons. The cell then diverts the electrons into an external circuit—producing the electricity. Meanwhile, the protons pass through a semipermeable membrane and combine with oxygen in the presence of a second catalyst, making water and heat.

Almost every year, the efficiencies of the catalysts are being improved. But in 2011, the cost of hydrogen fuel cells still exceeds the cost of gasoline engines. Continued improvement in fuel-cell technology and especially the development of better catalysts, along with a long-term increase in the price of hydrocarbons, will drive us to eventually adopt a hydrogen economy.

At the other end of the universe, equally interesting chemical developments are unfolding. The Hubble telescope, placed into orbit from the space shuttle in 1990,

has provided extraordinarily clear photographs of galaxies far beyond our own in the ultraviolet, visible, and near-infrared parts of the electromagnetic spectrum. Aside from being spectacularly beautiful, Hubble's images have already provided two generations of astronomers with new data that has revealed unexpected information about supernovae, the discovery of dark matter, the formation of stars, information about the big bang from images of the farthest and oldest galaxies ever seen, and evidence of distant planets and black holes. The examination of the spectral data from Hubble allows astronomers to identify the chemical components of distant sites, determine their temperatures, and examine their velocities. The spectra observed are in some cases identical to the atomic line spectra that led to the development of the quantum theory.

Sometime before 2020, NASA expects to launch the James Webb Satellite, a cousin to Hubble, but one that will focus its attention from the visible region of the spectrum farther into the infrared than Hubble. The infrared portion of the spectrum involves photons that are lower in energy than the visible photons. It is expected that these low-energy photons will reveal information about the first bright objects that formed in the universe, will reveal information about how galaxies evolve, will show new information about the formation of planets, and will provide the opportunity to search for the molecules of life that are hypothesized to exist in solar systems.

Chemists in the twenty-first century are optimistic that chemistry will continue to revolutionize our lives. The history of chemistry, compared to the history of man, is short, but distinguished. The benefits of clean water, abundant food, warm homes in winter and cool homes in summer, electronic gadgets of every kind, and medical treatments for a host of diseases have been made possible through chemistry. Each day we better understand the costs of misusing chemistry and the costs of treating by-products as waste. The next century of progress is limited only by our imagination.

A multitude of galaxies are visible in this portion of an image produced by the Hubble Space Telescope "Ultra Deep Field" project taken during the period from September 24, 2003, to January 16, 2004.

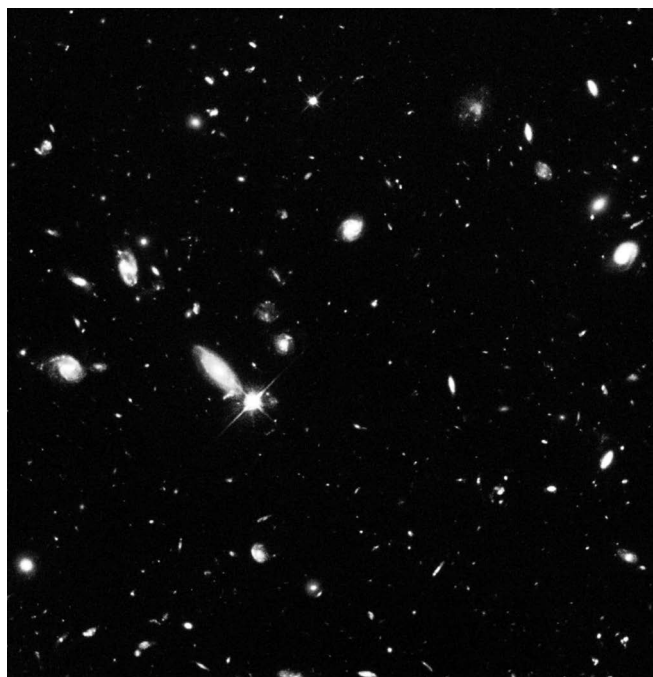


Image courtesy of NASA, ESA, S. Beckwith (STScI), and the HUDF Team

## For Greater Understanding

### Questions

1. Green chemistry
  - a. advocates using only plants as raw materials.
  - b. advocates the complete cessation of all synthetic chemical processes.
  - c. advocates reform of chemical processes to prevent pollution.
  - d. is irrelevant in most chemical industries.
2. Nanotechnology is concerned with
  - a. molecules that are 1 to 100 nm in dimension.
  - b. solids that are 1 to 100 nm in dimension.
  - c. new materials that are 1 to 100 nm in dimension.
  - d. all of the above.
3. Spectroscopy is
  - a. the study of the interaction of light and matter.
  - b. the study of stars other than the sun.
  - c. only useful to astronomers.
  - d. the study of colored molecules.

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