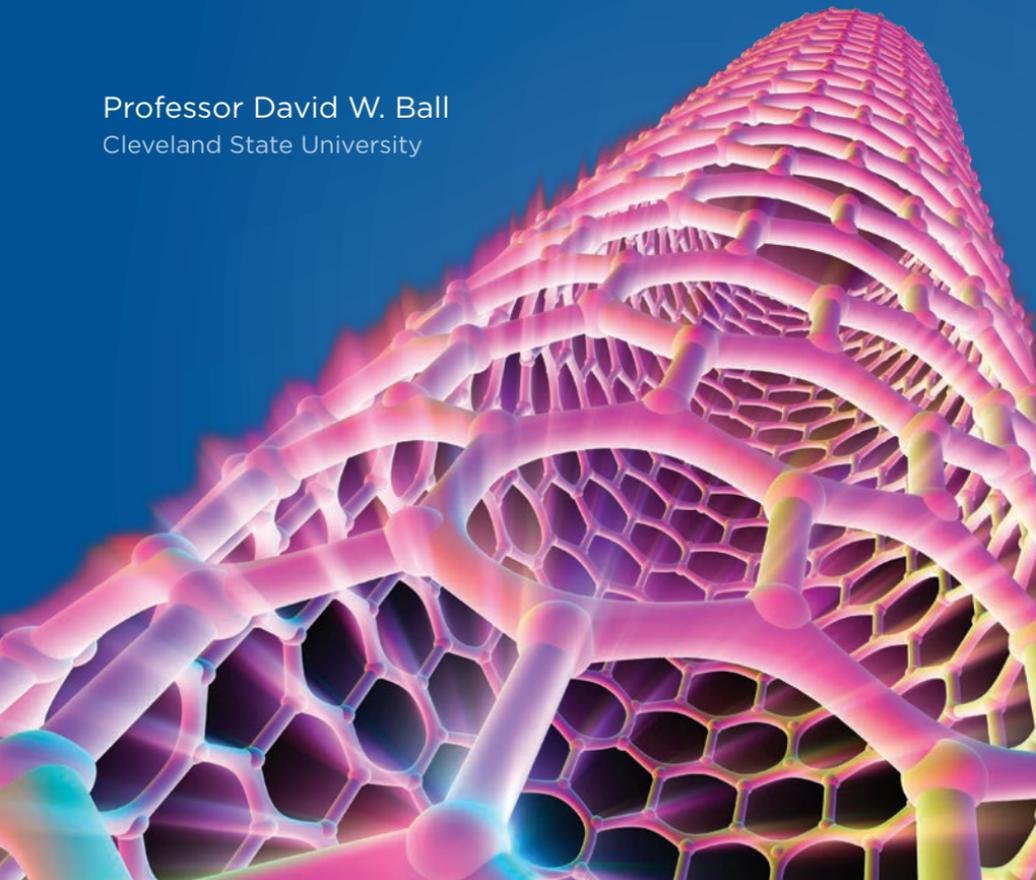


# The Nature of Matter: Understanding the Physical World

Course Guidebook

Professor David W. Ball  
Cleveland State University



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## David W. Ball, Ph.D.

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**P**rofessor David W. Ball is a Professor of Chemistry at Cleveland State University in Ohio. He received his bachelor's degree from Baylor University and his master's and doctoral degrees from Rice University. After performing postdoctoral research at Lawrence

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Professor Ball teaches various types of entry-level chemistry and physical chemistry in the undergraduate and graduate programs. His research interests focus on topics in computational chemistry, including new high-energy materials and small-molecule-protein interactions. He has more than 200 publications to date, half of which are research oriented and half of which are more educational in nature. He also has authored or coauthored a number of books, including a physical chemistry textbook (translated into Spanish and Japanese) and a book on math review for introductory chemistry students.

Professor Ball has received accolades for his teaching at the department, college, and university levels and recently served as a Distinguished Visiting Professor at the United States Air Force Academy in Colorado Springs, Colorado.

Professor Ball is active in the American Chemical Society at both the local and national levels. If he has any spare time, he does woodworking and takes weekly horseback-riding lessons. ■

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# The Nature of Matter: Understanding the Physical World

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## Scope:

The physical world around us is dominated by two obvious things: matter and energy. There are also some subtler components of the universe that impact how it works. It's the interaction of all these components that gives matter all of the mundane and unusual properties that it exhibits.

In the past 200 years, our ability to manipulate and even design matter with certain specific properties has dramatically increased and, in doing so, has had a substantial impact on progress. In some cases—for example, the use of wood and concrete as building materials—the matter we use has been around for centuries, even millennia. In other cases—for example, the use of semiconductors—the application of a particular form of matter is so new that we can remember a time when it wasn't invented yet.

This course is a presentation of the types of matter: what they are, how they behave, why they behave that way, and what they're used for. Wood, concrete, and semiconductors are all general types of matter, but they are used by society in very different ways. Polymers, fuels, solutions, and even food are other types of matter that we experience every day—of course, for different purposes, and those purposes are sometimes dictated by the particular type of matter.

The course begins with an introduction to three crucial components of the universe: matter, energy, and entropy. While most people are familiar with matter and energy, entropy is a less common topic—but it's just as important.

Next, you will explore atoms and molecules, as well as the rules of quantum mechanics that govern their behavior. In addition, you will discover how protons, neutrons, and electrons are organized in matter and even how atoms of different elements are formed in stars. The rules of quantum mechanics are explained in a straightforward way, with little or no math, but with a focus on how they explain the structure and properties of atoms and molecules.

The remainder of the course focuses on either a type of material or a property of materials. The types of materials presented include ionic and covalent compounds, solutions, organic compounds, polymers, superconductors, and semiconductors. Each of these types of compounds shares not only certain similarities but also certain applications in our society. For example, our society depends on electricity for much of its energy needs, and the electrical properties of semiconductors can be tailored to satisfy those needs much less expensively than older technology could. We also have the ability to take two dissimilar materials and combine them into a composite material whose physical properties are much more useful than the original. In this way, we can make products that are stronger and lighter than before.

The properties of materials dictate how we use them. For example, the use of composite materials allows us to construct stronger, lighter, and safer objects for everyday use. All solid and liquid materials have surfaces, and you will explore how the surface of an object affects its properties. In addition, there are different effects when these surfaces come into contact with each other, and you will explore how surfaces interact with similar and different surfaces. This particular topic can become rather personal if it involves an implant in a human body, such as tooth and bone replacement or artificial joints, and you will explore the implications for materials in these cases.

Finally, this course looks both backward and forward to examine materials that did and should define our society. Historians generally separate human progress into ages based on the dominant material of the time, whether it is stone, bronze, iron, or even plastic. You will discover why there was a natural progression from one material to another in some, but not all, societies. The course ends with a wish list for materials that don't currently exist but whose development should have a positive impact on our lives.

This course explores some of the fascinating ways that matter exists in our world. Some of the matter is naturally occurring, while other matter is manufactured. In either case, this course examines how society has both adopted and adapted various forms of matter so that human beings can have longer, happier, safer, and healthier lives. ■

# Matter, Energy, and Entropy

## Lecture 1

**M**atter is a key component of the universe we live in. Throughout this course, you will learn about matter and some of its wonderful forms and functions. Most of the time, energy will be hiding somewhere in the background, exerting its unwavering influence. Every once in a while, entropy will be the driving force for matter's behavior. In this lecture, you will learn about how the interactions of matter, energy, and entropy govern the nature of the universe.

### What Are Matter, Energy, and Entropy?

- Matter is anything with mass that takes up space. Most of what we see is matter—and a lot of what we don't see, including the air we breathe. The study of matter and how it interacts with other matter and with energy is chemistry. The nature of matter is controlled by three things: matter, energy, and entropy. The interaction of energy or entropy with matter determines how matter behaves.
- Energy is the ability to do work—or the ability to move matter around. Electrical energy moves electrons around in electronic circuits; mechanical energy moves gears, levers, screws, and wheels; gravitational energy moves mass toward the center of another mass; and wind energy moves great windmills. Without energy, we can't move or manipulate matter.
- Entropy is a measure of the distribution of energy. All other things being equal, the universe prefers high entropy, or the wider distribution of energy. The problem is that most of the time, all other things aren't equal. So, it's sometimes difficult to see how entropy by itself affects the behavior of matter.
- In order to understand the nature of matter, we need to understand how matter interacts with matter, with energy, and with entropy. Some behavior is based solely on the matter itself—no interaction

at all. Color is an example. Lemons are yellow, and limes are green. Those properties are fundamental to the matter and not based on how the matter is interacting with other matter or energy.

- Some behavior is based on the interaction of matter with energy. Think of an egg in a frying pan. Left alone, the egg just sits there. But if you add a bit of heat—a form of energy—at a certain temperature, the clear stuff turns white, and the yellow stuff gets solid, resulting in a fried egg. But it wouldn't have become fried without the energy. Temperature is a basic measure of the energy of a substance. Add energy, and it gets hotter; remove energy, and it gets colder.
- What about the interaction of matter and entropy? Try a simple thought experiment. Take a small cup with about an inch of water in it. Place a single sugar cube in the bottom of the cup, and then put the whole thing in an insulated bag. The insulated bag keeps energy from moving in or out. But in only a few minutes, the sugar dissolves in the water. We gave it no energy to dissolve. Instead, the dissolving process was driven by the distribution of energy to as many of the sugar molecules as possible. So, dissolving the sugar was an entropy-driven process.
- A liquid crystal is a substance that has both liquid and solid properties. In the liquid state, the molecules are ordered randomly, with various energies—a state of high entropy. In some cases, though, the application of the tiniest amount of electrical energy causes the molecules to line up, making a state of lower entropy. In many cases when this happens, there's a certain optical effect: The liquid crystal has a different color. It may just be a darker shade of gray, but that's enough.
- Put some liquid crystals in between some filters and polarizers, and you can control the red-green-blue combinations that make color. You now have a liquid crystal display (LCD), a major type of flat screen display used on televisions, computer screens, and



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**Liquid crystal displays are ubiquitous in today's world of tablets and smartphones.**

other video devices. They have the advantage of using very small amounts of energy, so they're more efficient than older cathode ray tubes. But they also show how matter, energy, and entropy all come together to make a product that impacts our everyday lives.

### **The Physical and Chemical Properties of Matter**

- In general, there are two types of properties of matter: physical properties and chemical properties. Physical properties are properties that describe matter's very existence. For example, iron is very heavy; heaviness is a physical property of iron. Color, density, shininess, and roughness are all properties that you use to describe the physical appearance or behavior of matter. Even the way matter interacts with energy is a physical property. When you add enough energy to liquid water, it boils to become steam. That's a physical property of water.

- Chemical properties are more complicated. A chemical has a certain composition of atoms. When a substance changes its composition of atoms in the presence of another substance, or in the presence of energy, that's called a chemical change. For example, hydrogen gas interacts with oxygen gas to change these two initial substances into a new substance called water. This behavior of hydrogen toward oxygen, or oxygen toward hydrogen, is called a chemical property.
- Other chemicals react with oxygen, too; natural gas, mostly the chemical methane, also reacts with oxygen. But it makes different products when it reacts, so its chemical property toward oxygen is slightly different than hydrogen's. Hydrogen also reacts with other chemicals, including nitrogen, iron, sodium, ethylene, benzene, and others. It also reacts with energy.
- Every chemical has its own unique set of physical and chemical properties. That's what ultimately distinguishes one form of matter from another. And that's why it's important to understand the properties of all forms of matter. Some of those properties can be pretty useful.

### Creating New Materials

- Although modern chemistry is only about 200 years old, we now know enough that we can try to make chemicals that have certain desired properties. Suppose that we want a new dye that looks red. We know about what size and other properties a molecule needs to have a red color. We can synthesize it in the laboratory and test it. Does it look red? If so, we can test it for other properties, such as stability and toxicity, to see if it works as a new food coloring.
- But why do we have to test it? Why can't we know for sure that our new substance will look red? There are two reasons. First, matter is complex. Although all matter is made up of 100 or so different kinds of atoms, when these atoms come together, their properties aren't always predictable, even when the same atoms are involved.

- For example, the element carbon has two major forms. The most common form is called graphite, which is a black, flaky solid that crumbles pretty easily. The less common form of carbon is called diamond. High-quality diamonds are clear and very hard; in fact, diamond is the hardest known naturally occurring substance.
- Diamond has a very high dispersion, meaning that it sparkles in light very vividly, making diamonds a desirable gemstone. These properties are diametrically opposed to the properties of graphite, even though the two substances are pure forms of the same element. This is because of how the atoms are joined, or bonded, together. Because the carbon atoms are bonded so differently in these two substances, the resulting materials have completely different properties that would be difficult to predict with certainty.
- The second reason we need to test new materials is because the influence of atoms on a new substance can be very subtle. For example, the element silicon does not conduct electricity very well; it is normally considered an insulator, not a conductor. However, by intentionally adding an impurity at the level of one atom per billion silicon atoms, we get a slightly conducting sample of silicon called a semiconductor that can be used to make electronic devices.
- One part per billion is not a lot, but for a semiconductor, it is enough of an impurity to change the properties of silicon completely and support an entire industry. These subtle effects require that we be careful when we test new materials.
- The complexity and subtlety that accompany the development of new materials points out another factor: blind luck, also known as serendipity. As advanced as our understanding of modern materials is, sometimes we discover something completely unexpected that opens up a new world of discovery.

- For example, in 1938, New Jersey chemist Roy Plunkett was trying to synthesize new refrigerants for the growing refrigerator and air conditioning market. One of the chemicals he was using was tetrafluoroethylene gas, which has a chemical formula of  $C_2F_4$ , a very simple molecule. The metal gas tank he was using got clogged before it was empty.
- After sawing the container apart, Plunkett found that the inside of the tank was coated with a white, waxy solid. Subsequent tests showed that this waxy solid was actually  $C_2F_4$  that had polymerized into a plastic. This plastic was very energetically stable, meaning that it's chemically unreactive and very slippery. The formal name of this plastic is polytetrafluoroethylene (PTFE). We know it better as Teflon.
- The fact that it's very chemically unreactive means that very few chemicals react directly with Teflon, making it a great protective coating. It's one of the slipperiest compounds known, and it's also an excellent insulator and a rather soft material. Many pots and pans are coated with Teflon so that cooked food sticks less. Teflon is also very heat resistant, making it all the more useful for cookware. It's even being used to make replacement veins for transplant into the human body. And it was discovered accidentally.

### The Fundamental Elements of the Universe

- The presence and interactions of matter, energy, and entropy dominate our universe and our lives. Matter is composed of about 100 different types of atoms, there are several manifestations of energy, and there is only one entropy—but from this relative small number of building blocks, our entire physical universe is built.
- But it's only been in the last 200 years or so—since the industrial revolution, when we started building machines to do the work of humans and animals—that we've had the freedom to study how matter and energy and entropy interact and learn how we can manipulate them to our advantage. A lot of progress has been made in that time, and there's certainly a lot more ahead.

- But there may be a limit. In the last few decades, we've gone from macroscale to microscale, and lately we've been going into the nanoscale. Think about these different scales: The macroscale is what you can hold in your hand, and the microscale is what you can hold in a pair of tweezers. But you can only see the nanoscale with the most powerful microscopes, because the nanoscale is only slightly larger than atoms and molecules themselves.
- We've only begun to explore the nanoscale and have discovered some new and interesting behaviors. As we move forward, we will discover unexpected, unusual, exciting materials that will propel new technologies, build industrial empires, and create the future.

### Suggested Reading

Engel and Reid, *Thermodynamics, Statistical Thermodynamics, and Kinetics*, chaps. 1, 5.

Halliday, Resnick, and Walker, *Fundamentals of Physics*, chaps. 18, 20.

Silverberg, *Chemistry*, chap. 2.

### Questions to Consider

1. What is the difference between temperature and energy? Does it make sense to describe something as being cold but having a large amount of energy?
2. Can you give an example of entropy in everyday life?

# The Nature of Light and Matter

## Lecture 2

Science is all about learning how nature behaves so that we can modify matter and energy to suit our needs. And humanity excels at modifying matter and energy, more so than any other creature, now or ever. But before we can modify matter and energy efficiently, we have to understand them—a feat that turned out to be more challenging than you might think. In this lecture, you will learn all about the nature of matter and energy.

### Matter Is Discrete

- The word “atom” comes from the Greek word that means indivisible, and the theory that matter is composed of atoms dates back to the 6<sup>th</sup> century B.C.E. in India and the 5<sup>th</sup> century B.C.E. in Greece. But that was one of several ideas about the structure of matter; unfortunately, there was no direct evidence of matter as atoms.
- It wasn't until the early 1800s that enough evidence was collected to support the existence of atoms, and what we call the modern atomic theory was announced by John Dalton in 1803. Although there was some resistance to Dalton's ideas—especially because no one had ever seen an atom—over time, most people accepted that the modern atomic theory was correct, and the science of chemistry advanced significantly after that. Individual atoms were finally seen in the mid-1980s after some new technology was invented, and at this point no one seriously doubts the existence of atoms.
- However, matter is not continuous, as was long thought. Matter is composed of discrete, individual atoms. These atoms are so tiny that matter looks like it's continuous, and for the most part it acts like it's continuous, too. But when scientists started doing careful experiments with matter in the 1800s, they found that the only way to explain their results was if matter came in discrete, but tiny, pieces.

## Unexplained Phenomena

- The 19<sup>th</sup> century was a century of intense exploration of matter and energy as science expanded tremendously. During the course of these explorations, though, some phenomena were discovered that couldn't be explained by the science of the time.
- Many of the unexplainable phenomena that scientists found through the 19<sup>th</sup> century had to do with the interaction of light and matter. For example, in 1860, German scientists Gustav Kirchhoff and Robert Bunsen invented the spectroscope. In this device, light was split into a rainbow with a prism, and then the rainbow was sent through a slit that allowed a single color of light to pass through a chemical sample. The prism was rotated so that each color passed through the sample sequentially.
- As the light passed through the sample, the sample absorbed certain colors of light but let other colors of light pass through unaffected. A plot of the absorption of light versus its color is called a spectrum. Kirchhoff and Bunsen noted that the different elements all had different spectra, suggesting that a spectrum is a way to identify elements apart from each other.
- In a similar setup, a sample was heated in a flame, and the light given off by the flame was passed through a prism and displayed. In this case, the sample actually emitted only certain colors of light but not others; the colors emitted were exactly the same colors that were absorbed in the original setup. Again, the specific colors emitted were characteristic of the elements making up the sample.
- The element hydrogen had a particularly simple spectrum, which made sense—hydrogen was already known as the simplest element. But why do elements have characteristic spectra, and why was the spectrum of hydrogen so simple and regular? Scientists at the time could not explain this relationship between light and matter.

- Another mystery of light involved its emission by a hot piece of matter. Hot objects emit light. Scientists assumed that all colors of light would be given off equally, because there is no reason to believe that any one color is given off preferentially. A graph of intensity versus color should therefore look like a straight line.
- Instead, when scientists actually measured the intensity of emitted light versus color, they found a graph that looked like a misshapen camel's hump, with some colors of light more intense than others. Clearly, there is a preference for some colors over others, but scientists could not explain why.
- At this time, light was known to be a wave. Throughout history, it was argued whether light was a wave or a tiny particle. Isaac Newton favored a particle nature to light, and he was fairly influential—but he was wrong. Light is a wave. That was demonstrated in 1801 by English scientist Thomas Young, who showed that light experienced constructive and destructive interference, just like water waves do.
- As a wave, light has certain properties: It has a wavelength, or the distance between two waves, and it has a frequency, or the number of waves that pass by a point every second. For any wave, including light, the velocity of the wave equals the frequency times the wavelength.
- In the mid-1860s, Scottish physicist James Clerk Maxwell deduced that the speed of light in a vacuum was a constant—and it's a very large constant: 186,282 miles per second. In our current theory of physical space, nothing can travel faster than a wave of light. With this in mind, scientists of the 19<sup>th</sup> century were trying to explain why light interacted with matter the way it did. But all of their attempts to develop a model failed.

## Max Planck

- Max Planck was a German physicist who specialized in thermodynamics, the study of energy and matter. He began studying the light intensity issue in 1894. After several failures, in the late 1900s, he came up with an idea that actually seemed to work.
- Planck considered the atoms in the glowing matter and thought about them as little oscillators, wiggling back and forth with a certain frequency. Planck wondered what would happen if the energies of these little oscillators were related to the frequency of the oscillation.
- In modern terms, Planck was proposing a simple mathematical formula:  $E = h\nu$ , where  $E$  is the energy of the oscillator,  $\nu$  is the frequency of the oscillator, and  $h$  is a proportionality constant now known as Planck's constant. When Planck made this assumption and applied it to glowing objects from a thermodynamics perspective, he was able to derive a mathematical formula whose plot agreed perfectly with the intensity of light given off by a glowing piece of matter.
- Everyone agreed that Planck's equation works, but there was disagreement on what Planck's assumption meant—the assumption that energy was related to frequency, that is. If we think of a wave as a simple up-and-down motion, then the distance between the top and the bottom of the motion is called the amplitude. Classically, the energy of a wave is related to its amplitude: A louder sound wave has a larger amplitude than a softer one.
- But this is not so for these little atomic oscillators, according to Planck, who was proposing that the energy of these oscillators is related to their frequency, not their amplitude—that is, the energy of the oscillators was related to the number of back-and-forth wiggles each second, not the amplitude of the wiggle.

- Planck's colleagues were a bit skeptical—this went against everything they understood about the behavior of waves. Some thought that Planck's assumption and derivation were just mathematical tricks. Even Planck himself, to some extent, was a bit skeptical. But it turns out that he was right.

### Albert Einstein

- Albert Einstein was another German physicist who, until 1905, was invisible to the scientific community. But in that year, he published a few papers on different topics, each of which rocked the physics world. One of them involved Planck's hypothesis relating energy to frequency, not amplitude. It was related to a phenomenon called the photoelectric effect.
- When you shine light on a metal surface that is kept in a vacuum, under certain conditions electrons are given off. This is called the photoelectric effect, and its trends are unusual. If you increase the intensity of the light, more electrons are given off, but they don't come off faster, with more kinetic energy. On the other hand, if you increase the frequency of the light that you use, the same number of electrons is given off, but they come off faster, with more kinetic energy. Finally, below a certain frequency of light, no electrons are given off.
- The photoelectric effect was discovered by German scientist Heinrich Hertz in 1887, but he and others weren't able to explain why it occurred and why it showed such trends versus the frequency of light. In fact, the photoelectric effect and the trends in its behavior was another unexplainable phenomenon related to light that was discovered in the 19<sup>th</sup> century.
- Einstein proposed that it wasn't just Planck's atoms that had an energy proportional to their vibrating frequency. He proposed that the energy of light itself was related to its frequency. That is, the energy of a light wave was fixed; it was determined by its frequency, not its amplitude.

- When a quantity is fixed, we say that the quantity is quantized. Light, Einstein proposed, was behaving as if it were a fixed package of energy, depending on what its frequency was, so the energy of light is quantized. What this also means is that because different colors of visible light have different frequencies, different colors of light have different energies.
- By suggesting that the energy of light was determined by its frequency, Einstein explained the photoelectric effect. His ultimate conclusion was that the energy of light was quantized. Einstein's proposal was initially looked upon skeptically by his colleagues, but eventually it took the scientific world by storm. Einstein's ideas of light were so basic to our knowledge of not just light but the rest of the universe that he won the 1921 Nobel Prize in Physics.
- Because light has a specific amount of energy depending on its frequency, light is acting like a little particle of energy. But light is also acting like a wave: It has wave properties, such as frequency and wavelength, and it refracts and diffracts, just like all waves do. The idea that light has both wave properties and particle properties is called the wave-particle duality of light.
- Previously, it was thought that something could be either a particle or a wave, but not both. The modern understanding of light argues that something—in this case, light—can have both particle properties and wave properties at the same time. This shift in viewpoint would also have dramatic effects on our understanding of the nature of matter in the mid-1920s.

### **Light as Both Wave and Particle**

- There are some important implications of Einstein's idea that the energy of light is related to its frequency that we experience in our everyday lives. Visible light, the light we see, consists of light between frequencies of a thousand trillion waves per second and about 500 trillion waves per second. Blue light has the highest energy while red light has the lowest energy.

- But the light we see isn't the only type of light there is. There's light we can't see, too. Going to lower frequencies—lower energies—we have infrared light, and then microwaves, and then radio waves. These low-energy forms of light can be detected by electronic circuits, but their interactions with matter are very different, and much lower in energy, than the interactions of matter with visible light.
- The higher-energy types of light—ultraviolet light, X-rays, and gamma rays—can interact with matter, too, but not by just twisting chemical bonds around. Instead, they have enough energy to completely break chemical bonds, which is usually not good for our health. So, we have to be careful when exposing ourselves to them.
- The entire range of light is collectively called the electromagnetic spectrum. They are all forms of light, but with varying wavelength, frequency, and energy. The values of these three characteristics vary smoothly, so these properties are continuous. But for any given wavelength, for any given frequency, the energy of that wave of light is specific. It cannot be different; it comes in a fixed amount. So, at its most fundamental level, energy is discrete—a fact that had a major impact on science as it developed in the early 20<sup>th</sup> century.



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**Low-energy forms of light, like the infrared light in a remote control, can be detected by electronic circuits.**

### Suggested Reading

Ball, *Physical Chemistry*, chaps. 9–10.

Gribbin, *In Search of Schrödinger's Cat*.

Halliday, Resnick, and Walker, *Fundamentals of Physics*, chaps. 38–40.

The Official Web Site of the Nobel Prize, <http://www.nobelprize.org/>.

## Questions to Consider

1. Imagine that you have a one-by-one-inch square of aluminum foil. How many times do you think you have to cut it in half before you have a single atom of aluminum?
2. A microwave oven uses microwaves to heat food. Microwaves have a lower frequency than visible light. Can microwaves break chemical bonds? Mobile phones also use microwaves; can they break chemical bonds?

# A New Theory of Matter

## Lecture 3

In this lecture, you will learn that, like light, matter has wave-particle duality. We've come a long way from the time when science thought that something had to be either a particle or a wave. We understand now that these two properties aren't mutually exclusive. We also recognize that energy has a central role in how electrons behave at the atomic and molecular level, something we need to keep in mind as we try to understand the properties of atoms and molecules.

### The Hydrogen Atom and Its Spectrum

- The element hydrogen has a very simple spectrum. This makes sense because hydrogen is the simplest known element. But it's not just that the hydrogen atom is simple; it turns out that the hydrogen atom spectrum follows a simple pattern.
- In 1885, Swedish scientist Johann Balmer deduced a simple mathematical formula to predict the wavelengths of the visible-light lines in the hydrogen atom spectrum, and in 1888, his compatriot Johannes Rydberg generalized the mathematical formula for all regions of the spectrum. Because his expression is more generalized, it's called the Rydberg formula.

$$\frac{1}{\lambda} = R \left( \frac{1}{n_a^2} - \frac{1}{n_b^2} \right)$$

- In this formula,  $\lambda$  is the wavelength of the light being absorbed;  $R$  represents a constant that's the same for any line of light in the spectrum; and the two  $n$  variables represent whole numbers or integers, so any line in the hydrogen atom spectrum is related to the difference of two integers.

- Although Rydberg's formula worked, there was no fundamental theory that explained why it worked. And while every element had its own characteristic spectrum, simple equations could not be deduced for any other element—not even for helium, the second simplest element.

## Niels Bohr

- In 1900, Planck came up with his famous equation  $E = h\nu$  to help describe light given off by glowing objects, and in 1905, Einstein applied that equation to light itself to suggest that the energy of light is quantized.
- In the early 1900s, scientists began to figure out the structure of atoms. Scientists had already figured out that atoms were composed of smaller, so-called subatomic, particles—first the electron, then the proton, and then later the neutron. But how were these particles themselves arranged into atoms?
- Ernest Rutherford, a scientist working in England, devised an ingenious experiment. He took tiny particles coming off a radioactive sample, aimed them at a very thin metal foil, and observed what happened. Most of the particles went straight through the metal, as though it were empty space. Some of the particles were deflected off to the side, and a small number of particles were reflected straight back toward the source.
- Based on these results, Rutherford proposed a model for the atom in 1911. He proposed that the more massive protons and neutrons were collected into the center of the atom in a tiny structure called the nucleus. The nucleus has most of the mass of the atom. The tinier electrons occupied the space around the nucleus in orbits, defining most of the volume of the atom, even though most of this volume is empty space.

- This is called the nuclear model of the atom, and some parts of it are still accepted today—especially the part about the protons and neutrons in a central nucleus of an atom. The electrons do not circle the nucleus; this is an unfortunate oversimplification. However, this model was an important step forward.
- Building on this model, in 1913 a Danish scientist named Niels Bohr considered Rutherford’s nuclear model as it applied to hydrogen: a single proton in the nucleus, with a single electron in orbit around it. Bohr already accepted the fact that energy was quantized, but he took it a step further: What if the angular momentum—a measure of the rotational momentum of a rotating body—of the electron going around the nucleus were quantized? And, in particular, what if it were multiples of Planck’s constant, which, as it turned out, has the same units as angular momentum?
- What Bohr is suggesting is that angular momentum is proportional to  $nh$ , where  $h$  is Planck’s constant and  $n$  is an integer. Essentially, angular momentum is a multiple of Planck’s constant. Bohr is assuming that the angular momentum of the electron is quantized. He is assuming that the angular momentum of the electron in hydrogen could only have certain numerical values.
- Bohr made two more assumptions. The first is that the force between the oppositely charged proton and electron were perfectly balanced out by the centrifugal force of the rotating electron. In addition, Bohr argued that the only way an electron can go from one value of angular momentum to another is to absorb or emit light that has exactly the same energy as the difference in the two energies of the angular momentum values. This is called the Bohr frequency condition, and it is still valid today.

- With these assumptions, and the concept of quantized angular momentum, Bohr was able to algebraically derive a simple equation.

$$\frac{1}{\lambda} = -\frac{m_e e^4}{8\epsilon_0^2 h^3 c} \left( \frac{1}{n_a^2} - \frac{1}{n_b^2} \right)$$

- All of the items in the equation except three are physical constants of nature. The three that aren't are the wavelength of light ( $\lambda$ ) and two integers that relate to the amount of angular momentum of the electron. But it agrees perfectly with the Rydberg equation.

$$\frac{1}{\lambda} = R \left( \frac{1}{n_a^2} - \frac{1}{n_b^2} \right) \text{ Rydberg's equation}$$

$$\frac{1}{\lambda} = \underbrace{-\frac{m_e e^4}{8\epsilon_0^2 h^3 c}}_{=R} \left( \frac{1}{n_a^2} - \frac{1}{n_b^2} \right) \text{ Bohr's equation}$$

- Essentially, Bohr was able to model the spectrum of the hydrogen atom from simple physical principles. When a theoretical model agrees this well with experiment, something must be correct about the assumptions of the model. And the key assumption of Bohr's model is that the angular momentum of the electron in the hydrogen atom was quantized.
- There was one more conclusion of Bohr's model of the hydrogen atom. He demonstrated that light is not the only thing that had quantized energies. Atoms like hydrogen also had quantized energies. Bohr couldn't use his model to predict the spectrum of any other atom, even by modifying his equation to make it more complicated—and less elegant. But the crucial step had been taken: At the atomic level, energy is not the only thing quantized; angular momentum is quantized as well.

## Electrons Are Waves

- In the early 1920s, someone thought about the fact that light has wave and particle properties and then questioned whether matter can have particle and wave properties as well.
- French scientist Louis de Broglie took two equations for energy— $E = h\nu$  and  $E = mc^2$ —and brought them together. Instead of using the speed of light ( $c$ ), he used  $v$  for the velocity of the particle and got an equation that the wavelength of the particle was related to Planck's constant, the velocity of the particle, and the mass of the particle:  $\lambda = h/mv$ .
- The wavelength variable ( $\lambda$ ) here is called the de Broglie wavelength and is the wavelength of a moving piece of mass. De Broglie's equation implies that matter does have a wavelength, but we don't observe it because the value of  $h$ , Planck's constant, is so small—on the order of  $10^{-34}$ . Because Planck's constant is so tiny, the de Broglie wavelengths are also very, very tiny.
- But as mass gets smaller, the fraction in de Broglie's equation gets larger because mass is in the denominator, and when a denominator in a fraction gets smaller, the resulting fraction itself gets larger. When the mass in de Broglie's equation is as small as an electron, the de Broglie wavelength may be significant. We would have to treat the electron like a wave, not a piece of matter.
- Between 1923 and 1927, physicists at Bell Laboratories were studying nickel metal with electron beams and, without realizing it, diffracted electrons. This is significant because only waves diffract. This was the first experimental evidence that electrons did, indeed, behave as waves, and the resulting waves had wavelengths exactly as predicted by de Broglie's equation.
- There's no doubt that electrons behave as waves. What that means is that any fundamental theory of electron behavior must treat electrons as waves—and Niels Bohr's theory didn't do that. That was the reason that Bohr's ideas were only partially successful.

## The Development of Quantum Mechanics

- With the physical evidence that electrons behave like waves, we need a new model. This model has to treat electrons as waves, not as particles. In 1925 and 1926, German scientists Werner Heisenberg and Erwin Schrödinger did just that, working independently of each other. They used different mathematical formalisms, and the one used by most scientists was formulated by Schrödinger. In either case, this new model is called wave mechanics or, more commonly, quantum mechanics.
- Schrödinger proposed that the behavior of a particle of matter was described by a mathematical function called a wave function. Wave functions could be any function that is physically possible, such as a sine or cosine function, in one or two or even three dimensions. Wave functions are represented by  $\Psi$ .
- But, Schrödinger proposed, the wave function had to satisfy a very specific differential equation that we know as the Schrödinger equation.

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi = E \cdot \Psi$$

- The Schrödinger equation contains the variable  $E$ , which is energy. This means that energy has a central role in quantum mechanics.
- The Schrödinger equation is a type of math formula called a differential equation, and there are many techniques that mathematicians use to solve these differential equations. When we do this for a variety of systems in quantum mechanics, we not only find mathematical expressions for the wave functions, but we also find expressions or values for the energy. In almost every case, the energies are limited to certain values determined by some integer that we call a quantum number.

- If the energies are limited to certain values, we call them quantized. Quantum mechanics predicts quantized energies—it doesn't assume or propose or hypothesize them; rather, quantized energies are the results of quantum mechanics.
- Quantum mechanics also predicts other quantized variables, such as angular momentum. At the macroscopic level, it's easy to ignore or overlook these quantized values, but at the scale of an atom, we can't ignore these values. If we really want to understand matter, we need to accept the fact that things like energy and angular momentum can only have certain values.
- As strange as some of its conclusions are, quantum mechanics is still currently the best model we have of electronic behavior. And because electrons determine the chemistry of atoms and molecules, the nature of materials is ultimately determined by quantum mechanics, with energy at the center of it all.

### **The Wave Behavior of Matter**

- In addition to electrons, protons and neutrons behave like waves, but because protons and neutrons are about 2,000 times more massive than the electron, their wave properties are about 2,000 times smaller. But experiments confirm that protons and neutrons also behave like waves.
- Technically, atoms and molecules also behave like waves, but the increasing masses of atoms and molecules over single protons, neutrons, and electrons means that their wave nature gets more and more invisible to us—although waves of helium atoms have been used to study other matter. The wave nature of matter affects mostly the electron, but that affects atoms and molecules and how matter interacts with each other, so we can't ignore the wave nature of the electron.

- But there's another way we use electrons as waves—in electron microscopes. A regular microscope uses light waves and magnifies them with mirrors or lenses so that we can easily see tiny objects. However, a microscope is inherently limited by the wavelength of light used, so a light microscope can only see things that are about 300 nanometers across, barely enough to see the smallest bacterium.



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- Realizing that electrons behave like waves, two German scientists invented a microscope in 1931 that used electrons, using magnets as lenses. Within two years, engineers had built an electron microscope that had better magnification than a light microscope, and scientists began seeing things too tiny to see before. Today's electron microscopes have the ability to magnify objects up to 2 million times, which is almost enough to see large molecules like DNA.
- We've been able to get even better magnification from special types of microscopes called scanning tunneling microscopes—and even those are based on a quantum-mechanical effect called tunneling. And with scanning tunneling microscopes, we've finally been able to see individual atoms and molecules, confirming the modern atomic theory 180 years after John Dalton proposed it.

**Electron microscopes have a variety of applications in biology and technology research.**

## Suggested Reading

Atkins and de Sousa, *Physical Chemistry*, chaps. 8–11.

Ball, *Physical Chemistry*, chaps. 9–10.

Gribbin, *In Search of Schrödinger's Cat*.

Halliday, Resnick, and Walker, *Fundamentals of Physics*, chaps. 38–40.

The Official Web Site of the Nobel Prize, <http://www.nobelprize.org/>.

## Questions to Consider

1. Even though quantum mechanics isn't usually applicable to large objects, are there things in everyday life that are quantized—that is, are restricted to having certain values of anything?
2. Why do you think different types of light bulbs cast different-looking light?

# The Structure of Atoms and Molecules

## Lecture 4

**F**undamentally, matter is made up of atoms, which are composed of protons, neutrons, and electrons. The protons and neutrons are located in a central region called the nucleus, while the electrons are in orbit around the nucleus. But electrons are not arranged at random—nor, unlike Bohr and Rutherford’s simplistic planetary model of the atom, are they in fixed orbits like the planets. Instead, as you will learn in this lecture, electrons are grouped into shells, subshells, and orbitals. This electronic structure gives atoms and molecules their electronic properties, which in turn strongly influence their chemical and physical properties.

### Shells and Subshells

- In an atom, electrons are organized into orbital groupings called shells. Shells are labeled with a quantum number, an integer that starts at 1. This quantum number is called the principal quantum number. The higher the quantum number, the farther the electron is, on average, from the nucleus.
- Also, the higher the quantum number, the higher the energy of an electron in that shell, and quantum mechanics states that the energy of the shell is restricted to certain values—that is, the energy is quantized. In shell number one, the electron has the lowest energy, in shell number two it has a higher energy, and so forth.
- Electrons can move from shell to shell, but only if they either absorb or emit energy in the form of light or heat—but it has to be the right amount of energy. Assuming that the energy involved is in the form of light, in order to go to a higher-energy shell, an electron has to absorb light, and in order to go to a lower-level shell, an electron has to emit light.

- In addition, the energy of the light absorbed or emitted must be exactly the same as the difference between the energies of the two shells involved. Different energies of light mean different colors of light, so electrons in atoms can only absorb or emit certain colors of light. This explains why the different atoms have different absorption or emission spectra—one of the problems that 19<sup>th</sup>-century scientists couldn't explain.
- Quantum mechanics explains this. Hydrogen absorbs and emits certain colors of light because its electrons have certain quantized energy values, and that means that the differences in quantized energy values are also quantized.



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- The hydrogen atom has only one electron. Because of this, the energy of the electron is determined solely by the principal quantum number. This is why the spectrum of the hydrogen atom is so simple, and quantum mechanics predicts the exact same expression for the energies of the hydrogen atom that Bohr's ideas did. But quantum mechanics is a better model for electrons because it treats them as waves, whereas Bohr's theory didn't.
- When there's more than one electron in an atom, there's a new effect: The negatively charged electrons repel each other depending on how far apart they are. This means that even though the electrons may be in the same shell, if they are in different subshells, they will have different energies.

**Neon, hydrogen, argon, and mercury lamps are different colors because the different elements involved give off different energies—or colors—of light.**

- Subshells can also be labeled with a second quantum number called the angular momentum quantum number, because quantum mechanics predicts that the angular momentum of the electron is quantized as well.
- But for this second quantum number, rather than using numbers to label the value, we use letters; this keeps us from getting confused between the two separate quantum numbers. The first four labels, which are the most common ones, are (in order)  $s$ ,  $p$ ,  $d$ , and  $f$ . Within each shell, an  $s$  subshell has the lowest energy, a  $p$  subshell has the next lowest energy, and so forth.
- Because of the mathematics of quantum mechanics, the first shell is limited to one subshell, so shell number one only has an  $s$  subshell. The second shell is limited to two subshells, so shell number two has an  $s$  and a  $p$  subshell. The third shell has only three subshells, the fourth shell has four subshells, and so forth. Because of this trend, we can predict the number of subshells in a shell.
- For atoms with more than one electron, the exact energy of the electron depends on the shell and the subshell that the electron is in. This is why the spectra of atoms other than hydrogen are more complicated to explain. But, again, quantum mechanics explains this, so it's definitely a better model than Bohr's model.
- Any  $s$  subshell, no matter what shell it's in, has only one orbital. Any  $p$  subshell, no matter what shell it's in, has only three orbitals. A  $d$  subshell has five orbitals, while an  $f$  subshell has seven orbitals. So, the total number of orbitals in a shell depends on the shell number, which determines the number of subshells, each of which have a certain specific number of orbitals.
- Each orbital in a particular subshell is slightly different, because it turns out that an orbital in a subshell has a certain shape in three-dimensional space. The single  $s$  orbital is spherical in shape.

- A single  $p$  orbital looks like a dumbbell. There are three  $p$  orbitals in any  $p$  subshell. The three orbitals are oriented in different directions in space, which we can arbitrarily label the  $x$ ,  $y$ , and  $z$  directions. The orbitals themselves are identical to each other, just oriented differently in three-dimensional space.
- The  $d$  orbitals have the shape of double dumbbells, or rosettes, and the five  $d$  orbitals in the  $d$  subshell also have different orientations in space. In principle, this idea continues into the  $f$  subshell and further on.
- All subatomic particles—protons, neutrons, electrons, and other particles—have a property called spin. It's not that we know they're spinning around like a top; we can't even see an individual particle in order to tell. It's that they behave as if they were spinning, so we use the name "spin" to describe that behavior.
- Different particles have different, characteristic spins that can point in a certain number of directions. In the case of an electron, its spin can point in two and only two directions. We can call them "up" and "down," or "alpha" and "beta."
- In the mid-1920s, Austrian scientist Wolfgang Pauli proposed the idea that an orbital can only contain as many electrons as there are directions of spin. With the electron, that's two; thus, each orbital can only hold a maximum of two electrons.
- This understanding limits the number of electrons that can go into orbitals, into subshells, and into shells. For example, shell number one has one  $s$  subshell, which has one orbital. This one orbital can hold a maximum of two electrons, leading us to the conclusion that shell number one can only hold a maximum of two electrons. Shell number two has two subshells,  $s$  and  $p$ . The  $s$  subshell, like all  $s$  subshells, can hold a maximum of two electrons.

- But the three orbitals in the  $p$  subshell can hold two electrons each, for a maximum of six electrons possibly occupying the  $p$  subshell. Add these six to the two in the  $s$  subshell, and shell number two can hold a maximum of eight electrons. In shell number three, add 10 electrons that can occupy the five  $d$  orbitals, for a maximum possible population of 18 electrons—and so forth.
- Hydrogen atoms have a single electron that goes into shell number one, the  $s$  subshell, and the only orbital in the  $s$  subshell. Helium atoms have two electrons, and both of them can go into shell number one, the  $s$  subshell, and the only orbital in the  $s$  subshell.
- Some fundamental results from quantum mechanics include that the energy of the electron is quantized, and the angular momentum of the electron is quantized, but the location of the electron is not quantized. That is, we don't know the exact  $x$ ,  $y$ , or  $z$  position of any electron in an orbital.
- That's why the analogy of electrons behaving like planets around the Sun doesn't work. We cannot say exactly where the electron is. All we can do is map out a region of space where the electron is most likely to be. Rather than calling this an electron orbit, we call this an electron cloud.
- Quantum mechanics reduces our understanding of electron behavior to probabilities, not certainties. Modern scientists understand that this probabilistic nature of electron behavior is the best we can do at this level.
- An electron configuration is a sort of shorthand that scientists use to summarize the organization of electrons in an atom. Using this shorthand makes it easier for scientists to communicate which shell and subshell electrons occupy and what happens to electrons in atoms when chemical reactions occur.

- An electron configuration is just a list of the quantum numbers that the electrons have as they occupy shells, subshells, and orbitals. Most electron configurations only explicitly list the principal quantum number and the angular momentum quantum number—actually, a letter—and have superscripts giving the number of electrons in all of the orbitals of the subshell. For example, the electron configuration of hydrogen is  $1s^1$ . The electron configuration of helium is  $1s^2$ .
- Although there is a regular ordering of filling the shells and subshells with electrons, the order depends on the shell and the subshell type. Frankly, it gets a little messy, but the trend has been all mapped out, and the electron configurations of the remaining atoms are well known to scientists. In a simple way, these electron configurations illustrate how electrons are organized in atoms.

### Molecular Orbitals

- A molecule is two or more atoms connected together. The electrons in molecules are organized very similarly to atoms: into orbitals, called molecular orbitals. In the case of molecules, however, the orbitals cover the entire molecule—they don't just stay on any one atom. Think of molecular orbitals as being formed from combinations of atomic orbitals from the atoms that make up the molecule, which in turn makes up matter.
- That's not always true. Many molecular orbitals are virtually identical to the original atomic orbitals. But, technically, they're no longer atomic orbitals—they're molecular orbitals. One rule is that a molecule has as many molecular orbitals as their atoms have atomic orbitals to hold their electrons.
- For example, when we make a molecule of  $H_2O$ —water—from two atoms of hydrogen and one atom of oxygen, we need to count atomic orbitals: Each hydrogen atom has one orbital for its electrons, while the oxygen atom has electrons in a single  $1s$  orbital, a single  $2s$

orbital, and the three  $2p$  orbitals, for a total of five orbitals. One plus one plus five equals seven, so the water molecule needs seven molecular orbitals for its electrons.

- And another rule is the same: Each orbital can contain a maximum of two electrons, as long as the two electrons have different spin. Some molecular orbitals resemble the spherical, dumbbell, and rosette shapes of individual atomic orbitals, while others cover more than one atom—sometimes the entire molecule, which is why they're called “molecular orbitals.”
- Because the water molecule only has 10 electrons, only the five lowest-energy orbitals have electrons in them; the other two are present, but empty—just like what sometimes happens in atomic orbitals.
- One of the difficulties with molecular orbitals, though, is that they're different for every molecule. The molecular orbitals have to conform to the shape of the molecule, and because every molecule has a different shape, molecular orbitals are unique to each molecule. This makes it difficult to make many general statements about molecular orbitals. Investigating their properties is a focus of a lot of research among scientists, because the properties of molecular orbitals tell us a lot about the chemical and physical properties of the substance.

### Suggested Reading

Atkins and de Sousa, *Physical Chemistry*, chaps. 8–11.

Gray and Mann, *The Elements*.

———, *Molecules*.

The Official Web Site of the Nobel Prize, <http://www.nobelprize.org/>.

## Questions to Consider

1. What do you think atoms and matter would be like if the electron had three possible spins instead of two?
2. Modern scientists don't use a planetary model for electrons anymore. Can you explain the differences between a planetary model and the true model for the electron arrangement in atoms?

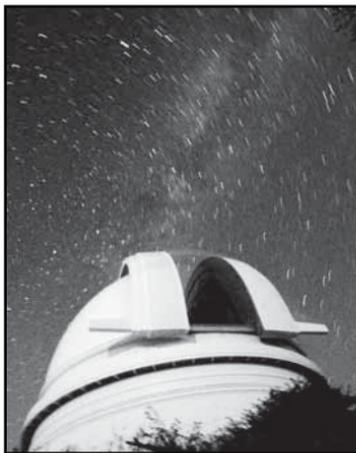
# The Stellar Atom-Building Machine

## Lecture 5

Humanity has benefited tremendously by manipulating matter and energy. But where did that matter ultimately come from? How were the actual atoms made? How did they get here? Scientists are pretty sure that they know the answers to these questions, and they have known them for about 100 years. What's interesting is that many of the people who first figured out the answers weren't chemists, or physicists, or even engineers. As you will learn in this lecture, they were astronomers.

### Telescopes and Spectra

- The telescope was invented around 1608 by some Dutch eyeglass makers. The Italian scientist Galileo heard about it a year later and promptly built his own much-improved model. Before the telescope, people had to rely on just their eyes to make observations. The telescope allows a user to observe things very far away, even into the outer reaches of the solar system.



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- Although the original telescopes used visible light, today scientists and engineers can construct telescopes using all parts of the electromagnetic spectrum. With these tools, astronomers can study the universe around us. One of their conclusions is that the element hydrogen makes up about 74 percent of the ordinary matter in the entire universe, the element helium makes up about 24 percent of the matter, and the rest of the 116 known elements make up only 2 percent of the matter in the universe.

- Astronomers know this by studying the light emitted by stars. Atoms give off or absorb only certain colors of light in a characteristic spectrum. By measuring those spectra on Earth, astronomers can compare them with a star's spectrum they get through the telescope. This allows them to know which elements are in the star.
- Using various data, astronomers conclude that 98 percent of visible matter is hydrogen and helium, the two simplest elements. Where did the other 2% of visible matter come from? The best answer comes from understanding how the universe itself evolved.
- The current theory of the history of the universe is called the standard cosmological model. Based on evidence from a wide variety of telescopes and from theoretical models, astronomers have deduced that the universe began about 13.7 billion years ago in an event called the big bang.
- The big bang wasn't really an explosion as much as the sudden appearance of space-time with an equivalent temperature of about a trillion degrees. In a billionth of a billionth of a billionth of a second, space expanded by a billion billion billion times, an expansion that continues to this day—although at a much slower rate.
- Mathematical simulations of these conditions predict that only certain elements were formed; this process is called primordial nucleosynthesis. Most of the matter—about 75 percent by mass—became hydrogen, formed by a single proton and one electron, while almost all of the remaining matter became helium. A tiny amount became deuterium, an isotope of hydrogen that has a proton and a neutron in the nucleus, and an even tinier amount became the elements lithium and beryllium.
- The rapid expansion of the young universe and its relatively rapid cooling kept other elements from being formed. And for the longest time, the entire universe was 75 percent hydrogen, 25 percent helium, and precious little else. This is actually not too different from the current elemental abundances in the universe.

- But where did the heavier elements come from? Earth is mostly oxygen, silicon, aluminum, and iron; hydrogen is only 0.15 percent of our planet, not 75 percent. In fact, these heavier elements came from stars.

## Gravity

- There are four fundamental forces in our universe: the strong nuclear force, the weak nuclear force, gravity, and the force due to electrical charge. Of these four, the strong and weak nuclear forces only act inside an atom's nucleus.
- The force due to electrical charge requires that there be an imbalance in electrical charge, either positive charge or negative charge. In addition, force due to charge can be attractive if the charges are opposite signs or repulsive if the charges are the same sign. Force due to electrical charge can also be nullified if an object has no net charge—that is, if an object is electrically neutral.
- Gravity is none of these things. It acts on all pieces of matter, big and small. It is purely attractive: All matter in the universe attracts all other matter in the universe. And it cannot be turned off.
- When the big bang spread matter across the universe, it did so ever so slightly unevenly, so the force due to gravity was ever so slightly uneven, and matter started to attract other matter unevenly. Eventually, a big collection of hydrogen and helium collected into a large cloud, contracting further and further under the influence of gravity. As the cloud of gases contracted, two properties increased: the pressure of the cloud and the temperature of the cloud.
- At some point, thanks to gravity, the temperature and pressure of the cloud got so large, and atoms got so pressed together, that the electrons in the atoms were ignored and atomic nuclei began to come together under the influence of the strong nuclear force. This is nuclear fusion, and a star is born.

- Nuclear fusion gives off a lot of energy, and the pressure generated by this energy halts the collapse of the cloud further for millions or billions of years. In nuclear fusion, atoms combine their nuclei to make larger nuclei, larger atoms. And the conditions aren't similar to those right after the big bang, when fundamental particles are trying to come together in the vast expanse of space. They can't—the space is too vast.
- In a star, however, the atoms are crowded together, brought together by the inexorable force of gravity. When nuclear fusion occurs in stars, larger atoms—larger elements—are formed. However, they aren't random formations, because different atoms have different stabilities.
- The current consensus is that the following nuclear fusion reactions occur. First, four hydrogen atoms fuse to become one helium atom. In order for that to happen, two protons must convert to neutrons. While it may seem strange that hydrogen will do this, temperatures and pressures are so high that nuclear processes like this are possible. In addition, energy considerations must be satisfied: Helium is an especially stable atom, and natural processes tend to favor energy stability.
- Under these conditions—not found in the big bang—hydrogen converts to helium. If a star is small enough, this is the only process that ever occurs, and the star (called a red dwarf) can last this way for billions or even perhaps trillions of years, which is longer than the age of the universe to date.
- If the star is massive enough, gravity continues to dominate. Eventually, the hydrogen starts running out, becoming scarce. Most of the star is now helium. Then, other nuclear fusion processes begin to occur: Three helium atoms fuse to become carbon atoms.

- This didn't happen in the big bang because the helium atoms weren't close enough for three of them to come together to make a carbon atom. We don't need to worry about protons becoming neutrons, because three helium atoms have just the right number of protons and neutrons to make a stable carbon atom.
- Eventually, the helium starts running low. Then, other nuclear fusion reactions begin to occur: Carbon begins to fuse with itself and remaining helium, eventually making atoms like oxygen, silicon, and neon.
- As a large star runs out of lighter elements, the remaining elements start fusing to make larger elements under the influence of gravity. As we get to larger and larger elements, the actual reactions become messier and more random, but eventually many of the chemical elements known to scientists get nucleosynthesized inside stars.
- Meanwhile, as these nuclear reactions occur, energy is constantly given off, the star continues to shine, and gravity continues its pull. Where does all this energy come from? It comes from mass. It turns out that the mass of a single helium atom is slightly smaller—only about 0.7 percent smaller—than the mass of four hydrogen atoms. There's a mathematical equation made famous by Albert Einstein relating the equivalence of matter and energy: Energy equals mass times the speed of light squared, or  $E = mc^2$ .
- When four hydrogen atoms fuse to make a helium atom, a huge amount of energy is given off as matter is converted to energy. But only up to a point. It turns out that nuclear fusion gives off energy until it makes the nickel 56 atom, which is a nickel atom with 28 protons and 28 neutrons. Making any larger atomic nucleus requires energy, and although a star is a great source of energy, it's not enough to make larger atoms.

- Also, nickel 56 is radioactive. It decays with a half-life of about 6 days into cobalt 56, which is also radioactive and decays with a half-life of 77 days into iron 56, which is stable. Thus, as a star generates its energy by fusing hydrogen to helium to carbon to other elements, eventually it all becomes atoms of iron.
- At this point, stuck at iron 56, there are two possibilities. In smaller stars, some of the fusions that normally occur also give off extra neutrons. These neutrons, one at a time, can be easily captured by other atoms in the star.
- The neutron-capture process continues, and over a period of millions of years, elements larger than iron can accumulate. This process is called the *s*-process of stellar nucleosynthesis, where the “*s*” stands for “slow.” Some of these larger elements can be vaporized into space and are called stardust, but it’s unclear what the ultimate fate of this matter is because the lifetimes of these stars is longer than the known age of the universe.
- There’s another possibility. When iron is being formed as the terminal part of fusion, if the mass of the star is greater than one and a half times the Sun’s mass, then there comes a point when the mass cannot withstand its own gravity, and the star collapses within a few seconds. During this collapse, protons and electrons are forced together to make neutrons.
- This sudden flood of neutrons sprays all of the heavier atoms, whose nuclei easily capture some, or even many, neutrons. Once again, these nuclei are radioactive, and neutrons decay into protons and electrons, making heavier elements. This process is called the *r*-process of nucleosynthesis, where the “*r*” stands for “rapid.”

- At the end of the sudden collapse, a huge shock wave is formed. This shock wave blasts the outer layers of the star off in a huge explosion called a supernova. Supernovas are among the most energetic events known in our modern universe. One supernova can outshine an entire galaxy with its sudden release of energy. The blast sends much of the non-neutron material out into space, while the remaining material degenerates into what is called a neutron star.
- All of the elements, even radioactive ones that have short half-lives, are spewed out by these explosions. We know this because astronomers can study the light given off by supernovas and identify the elements emitting or absorbing that light.
- Over billions of years, the material from ejected supernovas collects around the universe and, under the constant effect of gravity, collapses into another star. This time, however, the star is not just hydrogen and helium but has a small percentage of heavier elements as well. We know this from astronomers, who can get relative amounts of the elements in stars by studying the light they emit.
- Nuclear fusion is currently a topic of much research in high-energy physics. Humanity has been able to perform nuclear fusion, but mostly in the form of nuclear bombs that use the energy given off for destructive purposes. The goal of current research is to try to generate fusion in a controlled fashion, for useful energy purposes.

### Suggested Reading

Halliday, Resnick, and Walker, *Fundamentals of Physics*, chap. 42.

Hoyle, “On Nuclear Reactions Occurring in Very Hot Stars.”

———, “The Synthesis of the Elements from Hydrogen.”

## Questions to Consider

1. Which ultimate fate of the universe do you think is more likely: that the universe will eventually become a thin gas spread out all over or that the universe will eventually become one huge chunk of iron?
2. What do you think is happening to entropy as stars fuse hydrogen, helium, and other elements into larger atoms?

# The Amazing Periodic Table

## Lecture 6

Chemistry has a tool to help us organize some fundamental facts about the basic building blocks of matter, and it fits on a single page of paper. It's called the periodic table, and it is central to chemistry and the nature of matter. The fact that it incorporates so much, and helps us recognize so much about the elements, gives it a key role in science. How did it get this way? And, more importantly, why did it get this way? As you will learn in this lecture, it's all about the chemical properties of the elements.

### The Chemical Properties of Elements

- An element is a substance that cannot be broken down into simpler substances by chemical or electrical means. In 1913, English physicist Henry Moseley discovered what sets elements apart: The number of protons in the nucleus is different for each different element. The number of protons in an element is called the atomic number and is a fundamental concept in understanding matter.
- As elements were discovered through the passing of time, scientists began to notice that certain elements had similar chemical or physical properties. For example, sodium and potassium are two light metals that react rather violently with water and combine with the element chlorine in a one-to-one ratio. When the element lithium was first isolated in 1823 and its properties were investigated, scientists found that it reacted similarly to sodium and potassium.
- Other similarities were noted among other elements. The elements chlorine, bromine, and iodine showed similar chemical properties, as did the elements magnesium, calcium, and strontium. These similarities piqued the curiosity of some scientists.

- In 1829, German chemist Johann Döbereiner collected 15 elements into five groups of three based on their chemical similarities, which he called triads. Other chemists noted these similarities but were unable to make any real sense out of them.
- However, one other property did make sense in Döbereiner's triads: the atomic weight. The atomic weight is another fundamental property of an element. Originally, the relative weight of hydrogen, the simplest element, was set to 1, and the weights of the other elements were determined with respect to that standard. Döbereiner's triads showed that the atomic weight of the middle element was very close to the average of the other two elements in the triad.
- By 1860, about 60 chemical elements were known, enough for scientists to start organizing them. The big breakthrough came in 1869, when Russian chemist Dmitri Mendeleev published a chart of the elements that was the first version of the modern periodic table.
- Mendeleev organized his elements by atomic weights, as everyone else did, and in doing so argued that some atomic weights had to be wrong if the chemical properties were the organizing factor. It turns out that he was wrong on this.
- But Mendeleev did something that no one else did: He left gaps in his chart if an element didn't fit the correct progression of chemical properties. He reasoned that perhaps these elements hadn't been discovered yet, and based on the properties of other elements around them, Mendeleev predicted some of the chemical and physical properties of these missing elements.
- Mendeleev was right—six years later, the element gallium was discovered, and it had almost exactly the same properties that Mendeleev predicted. Not long after that, new elements scandium and germanium were discovered, and their properties agreed very well with Mendeleev's predictions. For these reasons, Mendeleev is generally considered the inventor of the periodic table.

## The Modern Periodic Table

- The modern version of the periodic table has seven rows. However, to make it appear legibly on a single page, a 14-column segment of the bottom two rows is cut away and placed underneath the remaining section, leaving an 18-column section behind. (See **Figure 6.1**.)
- Each row of the periodic table is called a period. The first period has only two elements: hydrogen and helium. The second row has eight elements, as does the third row. The fourth row has 18 elements, and so forth.
- Each column of the periodic table is called a group or a family. The elements in each group have similar chemical properties—the whole reason behind the periodic table. Some of the groups have names; for example, the first group is called the alkali metals.
- Groups are also labeled with a numeral/letter combination, so the alkali metals are also called the Group Ia elements. The second column of the periodic table is called the alkaline earth metals, or the Group IIa elements. On the other side of the table, the next-to-last column of elements is called the halogens, while the last column of the periodic table is called the noble gases, because they don't like to interact, or chemically react, with other elements.
- Originally, the developers of the periodic table ordered the elements in terms of atomic weight. But the order in the periodic table is not based on atomic weight; it's based on atomic number, the number of protons in the nucleus. Although the atomic weight does go up with atomic number, in six places it's the case that the lower-atomic-numbered element has a higher mass than the next element. This is because of the characteristic number of neutrons in the nuclei of each element, which does not follow a specific pattern from element to element.



- Why does the periodic table have this strange shape? Why does the first period only have two elements, the second period only have eight elements, and so forth? The answer is electron configurations. Quantum mechanics gives us rules for how electrons are organized in atoms. As these rules are followed, the elements and their properties just naturally form the shape of the periodic table.
- How does the periodic table explain why elements in the same columns have similar chemical properties? This is because of valence electrons, which are the electrons in the highest-numbered shell of an atom. Valence electrons are among the last subshells that are filled in an atom and are usually the farthest electrons away from the atomic nucleus.
- The elements in one column of the periodic table have the same number of valence electrons. In the first column, hydrogen has a single *s* electron in shell number one. Lithium has one *s* electron in shell number two; sodium has a single *s* electron in shell number three; potassium has one *s* electron in shell number four, and so forth down the column. They all have the same valence shell electron configuration, and therefore, these elements have similar chemistry.
- That's the point of the periodic table. They're all soft, shiny metals that react violently with water, that make compounds with chlorine in a one-to-one ratio, and so forth. Almost all chemistry happens because of valence electrons, because the valence electrons are farthest away from the nucleus, so they're the electrons that can interact with other atoms. Because these elements have similar valence shell electron configurations, they have similar chemistry.
- The same thing can be said about all of the columns of the periodic table. We've just explained something that Mendeleev knew but couldn't explain—why the periodic table works. Unfortunately, it had to wait until the development of quantum mechanics.

- With this understanding, we can make up some new labels to describe parts of the periodic table. In the first two columns of the table, the valence electrons are always going into  $s$  subshells. We call these first two columns the  $s$ -block of the periodic table. On the right side, the six columns there are where valence electrons are going into  $p$  subshells; we therefore call this the  $p$ -block of the periodic table.
- Similarly, we have the  $d$ -block, and the  $f$ -block is the section that we usually break away and place underneath the rest of the blocks. These labels emphasize our understanding of the subshell nature for the table's shape.
- The periodic table isn't perfect. There are anomalies in the electron configurations of some of the columns, especially when we get to larger and larger atoms in the  $d$ -block and the  $f$ -block. But these anomalies don't erase the overwhelming examples of similarities that do exist in the rest of the table. Ultimately, the table is backed up by quantum mechanics, which is currently the best model for understanding the behavior of electrons and atoms.

### Other Properties of the Elements

- There are other properties of the elements that the periodic table codifies, making it an even more useful tool. For example, atoms have size. In fact, it would take about 100 million atoms to make a line an inch long.
- We use X-rays to determine the approximate sizes of individual atoms, and it turns out that there's a trend that relates to the position in a period: As we move left to right across a period, the atom of the element gets smaller. Then, as we get to the next period by starting over on the left, the size of the atom jumps, and the size then decreases as we move across that next period. The trend isn't absolute, but it's obvious if you were to look at a graph or a picture of atomic sizes.

- Why does this happen? When you go across a row in the periodic table, you're staying in the same valence shell, the  $s$  subshell on one side and the  $p$  subshell on the other side. But as you go across the period, the number of protons—and therefore the nuclear charge—is increasing. This increase in positive nuclear charge attracts the negative electrons more, so the atomic size shrinks.
- On the other hand, when you start a new period, you're going to the next-highest shell, which is farther away from the nucleus. So, the size jumps up before shrinking again as you continue going across to the right. The periodic table embodies this so-called periodic trend of the sizes of the atoms.
- The periodic table also tracks some energy trends in atomic behavior. One key type of chemistry is the exchange of valence electrons among atoms. Atoms can either lose or gain valence electrons. There is an energy change that always accompanies the gain or loss of a valence electron.
- The energy change when an atom loses an electron is called the ionization energy. What's left over is a positively charged atom called a cation. Going across a period, as the nuclear charge increases, it gets harder and harder to remove an electron—that is, the ionization energy increases. Then, when you jump to the next shell by going to the next row, because the valence electrons are now farther away, it gets easier to remove them, and the ionization energy jumps down before slowly increasing again.
- As with atomic sizes, this trend isn't absolute, but it's pretty obvious if you look at a graph of ionization energies versus position in the periodic table.
- Other trends have been mapped out by scientists, all relating to the relative positions of elements in the periodic table. It's trends like these that make the periodic table the most useful one-page tool in all of science.

## Suggested Reading

Scerri, *The Periodic Table*.

## Questions to Consider

1. Modern science can do something alchemy can't: transmute elements. By using big atom smashers, scientists can make atoms of new elements. But this isn't alchemy, is it?
2. How important was Mendeleev's ability to predict new elements in blank spots of his periodic table?
3. Originally, scientists ordered elements by atomic masses, not atomic numbers. Consult a modern periodic table and try to identify all of the places where a heavier element comes before a lighter element.

# Ionic versus Covalent Matter

## Lecture 7

**T**here are a few different, major types of compounds in the world around us: ionic compounds and covalent compounds. In this lecture, you will learn about these two types of compounds—but, first, you will be reminded of how atoms are put together to make other materials. Then, you will learn about the individual characteristics of ionic and covalent compounds, as well as the differences between them, with examples of each type of compound.

### Electron Energies

- Electrons are organized into shells and subshells around atoms. The energy of the electrons depends largely on the shell number, and somewhat on the type of subshell. The higher the shell number, the higher the energy of the electron.
- Electrons are negatively charged, while atomic nuclei contain the protons that are positively charged. Positive and negative charges attract each other, and the conventions of physics state that attractions cause the energy of the system to go down—that is, become more stable.
- Scientists typically consider the zero point for energy at that point where the electron and the nucleus are very far away. As the electron approaches the nucleus and takes its place in a subshell, its energy decreases—that is, it gets negative. It's not energy that's negative; it's the change in energy when the electron joins the atom that's negative.
- When an electron is in the  $1s$  subshell, it's in the lowest energy—that is, the most negative energy with respect to being apart from the nucleus. When electrons occupy higher-numbered shells and subshells, their energy is higher, or less negative.

- The higher the energy the electron is, the easier it is to remove it, which is what we know about electrons in shells and subshells. It's important to understand that lower energy and higher energy actually means more negative energy changes and less negative energy changes, respectively.
- Although the exact energy of an electron depends on both the shell number and subshell type, the most influence on the energy of an electron is the shell number. The highest-numbered shell of electrons in an electron configuration is called the valence shell of electrons.
- Electrons in the valence shell are easiest to move around among atoms because they need the least energy to move, while atoms closer to the atomic nucleus require more energy to move around. This means that when atoms interact with each other, the interactions occur through the valence electrons, leading to the idea that virtually all chemistry is caused by valence electrons.

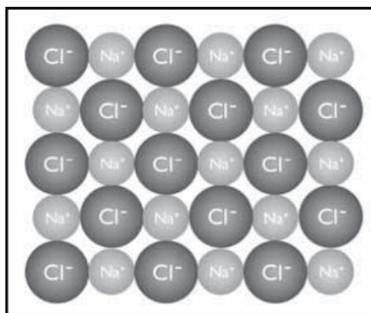
### **Ionic Compounds**

- A compound is a chemical combination of two or more elements to make a form of matter that has its own chemical and physical properties. For example, the elements sodium and chlorine can combine to make the compound sodium chloride, which has completely different properties from the elements it came from.
- There are two major ways that atoms interact to make compounds: by transferring valence electrons or by sharing valence electrons. When electrons are transferred, charged atoms called ions are formed, so the resulting compounds that are formed are called ionic compounds.
- During some chemical reactions, atoms can either lose or gain electrons. When an atom loses one or more electrons, it loses negatively charged particles and, therefore, becomes positively charged. A positively charged ion is called a cation. When an atom gains one or more electrons, it becomes negatively charged and is called an anion. Atoms typically lose or gain a characteristic number of electrons and thus take on a characteristic charge.

- But how do we know how many electrons an atom gains or loses? It helps to look at the original electron configuration of the neutral atom. For example, sodium atoms have 11 electrons: two in the  $1s$  subshell, two in the  $2s$  subshell, six in the  $2p$  subshell, and the final one in the  $3s$  subshell. Overall, then, the electron configuration of sodium is  $1s^2 2s^2 2p^6 3s^1$ .
- When sodium loses one electron in a chemical reaction, it loses the single  $3s$  electron in its valence shell. When it does, it takes on a net positive charge, and we give it the symbol  $\text{Na}^+$  to represent this cation. When it loses that single  $3s$  electron, what's left over is the remaining electron configuration:  $1s^2 2s^2 2p^6$ .
- Technically, the sodium can lose another electron, if there's enough energy available—it always takes energy to remove an electron from an atom. The problem is that now we're going to a lower-numbered shell, and when we go to a different shell, the energy change becomes much larger.
- In the case of sodium, it takes nine times as much energy to remove a second electron as it does the first. This amount of energy isn't usually available during the course of a chemical reaction, so sodium usually loses one and only one electron. The sodium cation has a characteristic charge of +1.
- The sodium atom starts with a single valence electron in the  $3s$  shell and loses only that electron to make an ion with a +1 charge. Because elements in the same column of the periodic table have the same valence shell electron configuration, all of the elements in the first column of the periodic table lose their only original valence electron to make cations with a +1 charge. Losing any more electrons than a single electron is just too energetically expensive.
- There is a tendency for stable ions to have complete valence shells. Because a complete valence shell has two  $s$  electrons and six  $p$  electrons, or a total of eight electrons, this tendency is called the

octet rule. Although there are common exceptions to the octet rule, the concept is a rule of thumb for helping us figure out what ionic charges can form.

- Basic physics says that opposite charges attract. When some atoms lose electrons and other atoms gain electrons, ions of positive and negative charges are formed. These oppositely charged ions attract each other, and when they do, they make an ionic compound. So, an ionic compound is a combination of positively and negatively charged ions. Sodium chloride, or common table salt, is an example of an ionic compound.
- Ionic compounds are typically very hard and brittle; they usually have very high melting points, and many of them dissolve in water. In addition, the total positive charge of ionic compounds is equal to the total negative charge, so, overall, any sample of an ionic compound is electrically neutral.
- It's not proper to refer to “molecules” of ionic compounds. Ionic compounds exist as ions that are held together by electrostatic attraction. In the solid state, the ions alternate: first positive ion, then negative ion, then positive ion again, then negative ion again, and so forth. This goes on in all three dimensions, making something called a crystal.
- So, the ionic compound exists as a certain ratio of cations and anions that can be listed in a chemical formula, such as NaCl for sodium chloride. But there are no discrete NaCl molecules; there are just alternating positive and negative ions. Sometimes we use the term “formula unit” for ionic compounds.



**Alternating positive and negative ions give NaCl its crystalline structure.**

## Covalent Compounds

- The octet rule is really all about trends in energy: When atoms have eight electrons in their valence shell, changing that number of electrons requires so much energy that it doesn't normally happen in everyday chemical reactions.
- For ionic compounds, one way for an atom to get to eight valence electrons is to either lose a few to become a cation or gain a few to become an anion. Another way for atoms to have a filled valence shell and satisfy the octet rule is by sharing electrons. When atoms share electrons, they stick together, making a chemical bond. This type of chemical bond is called a covalent bond, and compounds formed with covalent bonds are the second major type of chemical substance we recognize.
- Unlike ionic compounds, in covalently bonded compounds, individual molecules do exist, so it's proper to use the word "molecule." This is another difference between ionic and covalent compounds. Not only are the ways of making octets different, but also how the very compound exists is different. Ionic compounds exist as oppositely charged ions making a three-dimensional crystal, while covalent compounds exist as discrete molecules.
- Because all of the elements in fluorine's column, for example, have the same electron configuration, they can all form two-atom, or diatomic, molecules in their natural elemental state. They all share a single pair of electrons in order to complete the octets. This single pair of electrons is also called a single covalent bond.
- Under some circumstances, more than one pair of electrons can be shared. The oxygen atom, for example, has six valence electrons in its outermost shell. If we take a second oxygen atom and allow the two atoms to share two pairs of electrons, a total of four electrons, then each atom now has eight electrons around it, satisfying the octet rule. Sharing two pairs of electrons leads to what we call a double covalent bond, or just a double bond.

- In other circumstances, three pairs of electrons can be shared. For example, each nitrogen atom has five valence electrons. If two nitrogen atoms share six electrons, then there are eight valence electrons around each nitrogen atom, satisfying the octet rule. The sharing of three electron pairs, or a total of six electrons, makes a triple bond. We don't typically see anything more than a triple bond in common covalent compounds.
- Covalent bonds can exist between different atoms; indeed, this is where the vast number of covalent compounds comes from. An oxygen atom, for example, has six valence electrons and needs to share two more to have an octet. If it shares one electron each from two different hydrogen atoms, then the oxygen atom has eight electrons around it, while each hydrogen atom has two electrons around it. We've just constructed a stable covalent molecule—of water, H<sub>2</sub>O.
- We aren't limited to single covalent bonds. Many covalent compounds have double or triple covalent bonds when necessary to satisfy the octet rule. One example is carbon dioxide, a gas that's an important part of our atmosphere. The only way to satisfy the octet rule in all the atoms is to assume that the central carbon atom makes two double bonds, one to each oxygen atom on either side of it.

### The Variety of Covalent Compounds

- Because the octet rule is a guiding principle in making covalent bonds, certain atoms make a characteristic number of bonds, much like atoms make only certain specific charges when they form ions. The periodic table helps us; most of the elements that make covalent bonds are on the right section of the periodic table.
- Starting from the right-most column, the noble gases usually make zero covalent bonds—they usually don't make covalent compounds. In some unusual circumstances they do, but most of the time they don't. Moving over one column to the left, the halogens column, these elements usually make a single covalent bond. Moving over one more column, to the one with oxygen on the top, these atoms

generally make two covalent bonds, then three bonds for the next column, and finally four covalent bonds for the column of elements starting with carbon.

- There are exceptions to these rules, but the periodic trends in the number of covalent bonds preferred is a useful rule of thumb in figuring out the covalent bonds in a molecule. Using these rules of thumb, it's possible to make large and complex covalent molecules, especially when using carbon atoms as a backbone. Carbon is unique among elements by making strong covalent bonds with not just other carbon atoms, but also with atoms of other elements.
- This allows us to make large, complicated, three-dimensional covalent molecules. The DNA molecules in our cells are built using covalent bonds. Most of the proteins, carbohydrates, and fats in our bodies are covalent compounds as well.
- There are compounds that are both covalent and ionic in character. There are some ions that are themselves stable combinations of covalently bonded atoms, except that in these cases, the covalently bonded combinations have a net overall positive or negative charge. These so-called polyatomic ions can make ionic compounds like any other ion, forming substances that have both ionic and covalent bonds. An example is sodium bicarbonate, or baking soda.

### Suggested Reading

Silverberg, *Chemistry*, chap. 9.

### Questions to Consider

1. Do you think an ionic compound can be made from just two different anions or two different cations? Why or why not?
2. Thinking of the octet rule, why don't we expect to see quadruple bonds very often in covalent compounds?

# The Versatile Element: Carbon

## Lecture 8

In its elemental form and its compounds, carbon demonstrates a chemical versatility unmatched by any other element. The element carbon is central to life and has interesting and extreme properties as a material. In fact, graphite, diamond, fullerenes, nanotubes, and graphene are all types of pure carbon. In this lecture, you will learn about how this one element can demonstrate many different forms with very different properties—how this one type of atom can contribute to so many different materials.

### The Carbon Atom

- One of the reasons carbon is so versatile is because of the number of chemical bonds it makes. Unlike many elements in the periodic table, carbon rarely makes ions, either positive or negative. Instead, carbon tends to form covalent bonds.
- Because the carbon atom has only four valence electrons, it needs four more valence electrons to satisfy the octet rule. It accomplishes this by making four covalent bonds with up to four other atoms. It can make four single bonds to four other atoms, but carbon is one of the elements that can make double or triple bonds, too.
- One of the keys in understanding the versatility of carbon is in recognizing the structure of the bonds around a carbon atom. Because of the effects of quantum mechanics, the bonds that a carbon atom makes adopt different shapes if a double bond or triple bond is formed. That's because while the first bond a carbon atom makes forms a head-on overlap with another atom, the second and third bonds are formed by sideways overlap with the other atom.
- The result is that when a carbon atom makes covalent bonds with three other atoms, one of the bonds being a double bond, the other atoms make a planar triangle shape around the central carbon atom.

- When a carbon atom makes covalent bonds with two other atoms, with one of the bonds being a triple bond, the two other atoms line up on either side of the carbon atom, making a straight line. These types of bonding patterns add to the different ways carbon atoms can bond with other atoms.

### Carbon Allotropes: Graphite

- Assume that we're discussing just carbon the element. But we're not just talking about one type of substance. Even though we're only talking about one type of atom, in many cases, we can arrange those atoms in different ways, into different structures. Each type of structure that a pure element can have is called an allotrope. Carbon has several allotropes, each with rather different properties.
- The most common, energetically stable allotrope of carbon is called graphite. Graphite is a shiny, black solid that's rather soft and flakes apart easily. It's this last property that made graphite the writing part of a pencil.
- The structure of graphite explains a lot of its properties. Graphite is composed of flat sheets of carbon atoms that are bonded in a honeycomb pattern. Each carbon is making two single bonds and one double bond to a total of three other carbon atoms, which in turn are bonded to three carbon atoms, and so forth. The layers are not directly bonded to each other.
- Instead, the layers attract each other due to the constant movement of the electrons in the layers. Normally, such forces of attraction are weak, but because the layers are so large, the overall attraction keeps the layers stuck together. The distance between the layers is



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**The flaky quality of graphite is what makes it a great writing tool.**

about twice as far as the distance between atoms within a layer. This type of layered structure is mimicked by only a few other naturally occurring substances.

- Substances that have different physical properties in different directions are called anisotropic materials. Despite this anisotropy, one major use of carbon is as an electrode for several electric processes. Many batteries use graphite electrodes, and graphite is also used in components of steel mills because it is very heat resistant.

### **Carbon Allotropes: Diamond**

- Another allotrope of carbon is diamond, which is a crystal of the element carbon. Diamond is energetically unstable with respect to graphite and will decompose into graphite over time. Under normal conditions, “over time” means millions and millions of years, so if you have any diamond jewelry, it’s safe.
- Like graphite, the properties of diamond are largely caused by its molecular structure. Unlike graphite, where the bonds of the carbon atoms are flat, in diamond the bonds of the carbon atoms are three-dimensional, and every carbon atom is bonding to four other carbon atoms in an almost infinite network of covalent bonds. In fact, a perfect diamond can be considered one huge molecule, with unbonded carbon atoms only at the surface.
- Ironically, the individual carbon-carbon bond is weaker in diamond than it is in graphite. But breaking or melting a diamond would require breaking a lot of these bonds all at once, which would require a lot of energy, so diamond is the hardest naturally occurring substance known. Industry takes advantage of diamond’s hardness by using diamond dust and diamond powder as a polishing compound. And it’s not expensive; only gem-quality diamonds command high prices.
- Diamond is also a very good conductor of heat. In fact, it’s the best heat conductor known, conducting heat five times better than copper metal. There are several industries, such as the electronics

industry, that would love to take advantage of this property of diamond—imagine your computer processor never overheating because a layer of diamond wicks away the heat—but diamond is too rare and expensive to be used like this.

- The best gem-quality diamonds are absolutely colorless. That’s because in many substances, color is caused by unbonded electrons, and in a perfect diamond crystal, all of the electrons are bound up in covalent bonds between carbon atoms. Most, but not all, colored diamonds are considered undesirable. The colors are caused by impurities of non-carbon elements or by defects in the crystal structure of the diamond.
- In the United States, gem-quality diamonds are graded by color and appearance as well as size and shape. The most popular grading scale is put out by the Gemological Institute of America. Needless to say, the better the diamond is graded, the higher the price it commands. Fancy colored diamonds are graded on a different scale, and their pricing is much less standardized than uncolored diamonds.
- Diamonds are thought to be formed deep in the Earth’s mantle, where temperatures and pressures are much higher than we experience at the planet’s surface. Both organic and inorganic sources of carbon can be used to make diamond. Eventually, through volcanic processes, diamonds find their way to the surface, looking very unlike their polished versions.

### **Carbon Allotropes: Fullerenes**

- In the mid-1980s, researchers at Rice University in Houston, Texas, were studying the vapors given off by laser-blasted carbon. Under certain conditions, a cluster of 60 carbon atoms was a very popular product. The only way this would happen, of course, is if this cluster were energetically stable. The researchers proposed that these 60 atoms took on the shape of a soccer ball and proposed the fanciful name “buckminsterfullerene” for the cluster, after Buckminster Fuller, the inventor of the geodesic dome.

- In 1990, two German researchers successfully synthesized and isolated the  $C_{60}$  molecule—from soot. Experiments indicated that the soccer ball structure of the molecule was correct: The carbon-carbon bonds in the molecule showed the same pattern as the grooves on a regulation soccer ball.
- Essentially, buckminsterfullerene—also known as buckyball—is composed of 20 hexagonal, 6-membered rings of carbon connected by 12 pentagonal, 5-membered rings. Each carbon is making two single bonds and one double bond to three other carbon atoms. Even though each ring is flat, the molecule looks spherical, and it can be treated as spherical when modeling some of its chemical and physical properties.
- Although the 60-atom molecule is the most stable, other distorted-spherical molecules similar to buckminsterfullerene have also been isolated, including those with 70, 72, 76, and 84 carbon atoms. As such, the class of carbon molecules with spherical or somewhat spherical shape is called fullerenes.
- Fullerenes have some interesting properties. Perhaps the most obvious is that they surround a relatively large volume of empty space. Subsequent research on fullerenes has demonstrated that as many as four atoms can be encapsulated inside a fullerene. This suggests that larger fullerenes, with hundreds of carbon atoms, might be able to trap other molecules, such as drugs, and help transport them to their active sites in the body.
- Mixtures of fullerenes with metals, such as potassium, are superconductive at low temperatures—about 400 degrees Fahrenheit below zero. Buckyballs can also be reacted with hydrogen; in fact, there is speculation that fullerenes might be used for hydrogen storage in cars that run on fuel cells. To date, there aren't any practical or commercial applications for fullerenes.

## **Carbon Allotropes: Nanotubes**

- If you take a buckyball and add an additional ring of carbon atoms to it, the spherical molecule grows a bit in one direction. If you do that again, and again, and again—until you have a structure that is long, thin, and cylindrical—then you have made a nanotube. A nanotube can be thought of as a single sheet of graphite that has been looped into a tube. They're considered part of the fullerene family but have some completely different properties.
- Nanotubes were first investigated in the 1950s but rose to more widespread knowledge after the discovery of buckyballs. Carbon nanotubes have some of the most extreme mechanical properties of any material measured. Measurements put them at more than 300 times stronger than steel when trying to pull them apart, a measurement called tensile strength.
- Nanotubes can be either electrical insulators or conductors, depending on the size of the tube. Strongly conducting nanotubes can conduct almost 1,000 times more electricity than copper. They are also good thermal conductors, but like graphite, only in one direction: the long axis of the tube. Other measurements of their hardness suggest that they are even harder than diamond.
- There are two main problems with nanotubes: It's difficult to make nanotubes of a given tube size, and most nanotubes are very short. However, they can be made in large amounts by various methods, including laser vaporization of graphite and arc discharges using carbon electrodes. Nanotubes can be made in large enough quantities to use them in certain specialized applications.
- Unlike their fullerene cousins, nanotubes do have some uses, mostly as components in composite materials. By virtue of the fact that bulk nanotubes are a mixture of various sizes of tube, the overall mechanical properties don't come close to the extreme behavior of a pure, single sample.

- Even so, the properties of these nanotubes can significantly enhance the properties of the material. Most of the current uses of nanotubes are for items that benefit from increased structural strength, including bicycles, tennis rackets and golf clubs, skis, baseball bats, and skateboards.

### **Carbon Allotropes: Graphene**

- Graphite is composed of flat sheets of honeycombed carbon atoms that are weakly connected to each other. If you take the sheets apart so that you're working with a sample of graphite that's one atom-layer thick, then you've got something called graphene.
- Graphene can be thought of as two-dimensional carbon. Like carbon nanotubes, graphene was recognized for decades but not created in large amounts until the first few years of the 21<sup>st</sup> century. Like a nanotube, graphene is strong, about 100 times stronger than steel. However, being only one atom thick, graphene is very light. And it can be rather easy to make. Graphene is the most chemically reactive form of carbon, because the carbon atoms are uniquely exposed to other chemicals from both sides.
- The electrical properties of graphene are still being explored, but measured properties are already unusual because of the two-dimensionality of the substance. Although only one atom thick, graphene is visible to the naked eye because it absorbs a small amount of light, making it appear slightly gray. Thermally, graphene is a better heat conductor than diamonds or nanotubes.
- Like fullerenes, graphene has yet to be developed into any commercial product, but there are many suggestions being explored. Electronics, composite materials, optical devices, and even filters are being explored as possible applications for graphene.

## Suggested Reading

Bruice, *Organic Chemistry*, chap. 1.

Katsnelson, *Graphene*.

The Official Web Site of the Nobel Prize, <http://www.nobelprize.org/>.

## Questions to Consider

1. Diamond is less energetically stable than graphite. Why do you think diamond doesn't spontaneously change back into graphite?
2. The element silicon is right below carbon in the periodic table and also makes four covalent bonds. However, it doesn't have anywhere near the complex chemistry that carbon does. Speculate on why this might be so.

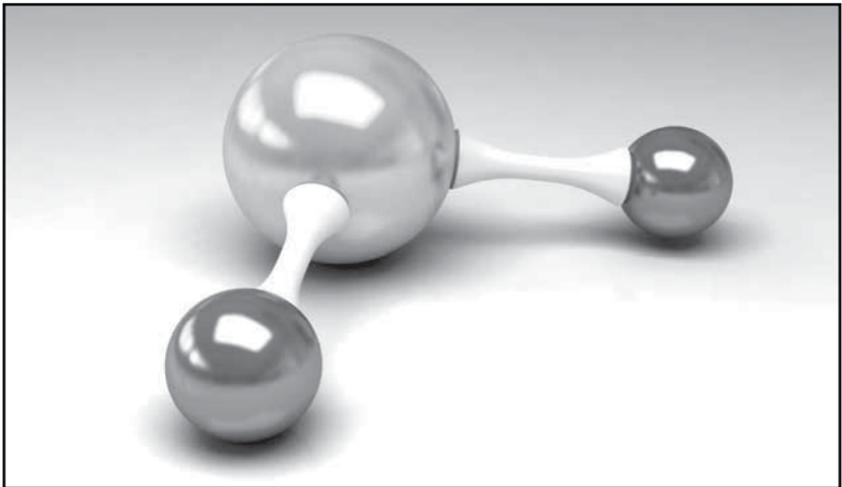
# The Strange Behavior of Water

## Lecture 9

**W**ater is weird. But it's so commonplace that it's difficult to realize that unless we really think about it. However, if it weren't for water's unusual properties, it's likely that we wouldn't be here to be thinking about it in the first place. As you will learn in this lecture, most of water's unusual properties come from its polarity and its hydrogen bonding, both of which impact the energy of interaction that water molecules have with each other and with other substances.

### The Structure of Water

- A water molecule ( $\text{H}_2\text{O}$ ) is composed of two atoms of hydrogen (H) and one atom of oxygen (O). The two hydrogen atoms are connected, or bonded, to the oxygen atom through covalent bonds, or electron sharing. A water molecule looks like a boomerang, with the oxygen atom at the corner and the two hydrogen atoms at the ends.



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The 104.5-degree angle of the covalent bonds in a molecule of water has a consequence—polarity.

- The water molecule is bent at an angle, and the angle between the two covalent bonds is about 104.5 degrees. There are consequences to having this bent shape. While a covalent bond is made by sharing electrons, the electrons aren't shared equally between the two atoms in the bond.
- The hydrogen atom has a single proton in its nucleus, so the overall charge on the hydrogen nucleus is +1. But the oxygen atom has eight protons in its nucleus, for a nuclear charge of +8. These eight protons attract the electrons much more strongly than the single proton in hydrogen, so the shared electrons of the covalent bond spend more time around the oxygen atom.
- This means that the sharing isn't equal. Because the electron has a negative charge and spends more time near the oxygen atom, the oxygen atom gets a slight negative charge to it. By contrast, because the electrons stay away from the hydrogen atoms, the hydrogen atoms get a slight positive charge.
- A covalent bond in which the electrons are unevenly distributed like this is called a polar covalent bond. Think of it as a tug-of-war, with one atom in the bond pulling electrons harder than the other atom. If these two polar covalent bonds were pointed directly opposite each other, their pulls would cancel out. But they don't in the water molecule; in  $\text{H}_2\text{O}$ , the two bonds are off to one side, making a bent structure. Because they don't cancel out, there is an imbalance in the electron sharing in the molecule as a whole, so the molecule is polar—not just the covalent bond.
- But these covalent bonds are even more noteworthy. Hydrogen's valence electrons are in shell number one, and oxygen's valence electrons are in shell number two. These are the smallest shells, so the electrical charge is confined to a fairly small volume around the atom—we say that the atom has a high charge density. Because of this, the polarity of this covalent bond is unusually high, so high that it affects the properties of the molecule.

- Basic physics says that opposite charges attract, so the positive end from one molecule can interact with the negative end of another molecule. But because the polarity of this bond is unusually high, the interactions between molecules are unusually strong.
- This type of interaction is called a hydrogen bond. Hydrogen bonds occur in compounds that have hydrogen atoms covalently bonded directly to nitrogen, oxygen, or fluorine atoms; all three of these atoms attract the electrons so much that a very polar covalent bond is formed.
- When positive and negative charges get close together, the energy of the system decreases, so a hydrogen bond causes additional stability between water molecules. In the case of water, the hydrogen bond energy is about five percent of a regular covalent bond energy. This may not seem like much, but each water molecule can attract two other water molecules and be attracted to two other water molecules. This allows a single water molecule to network with other molecules in a way that other molecules don't, or can't. These hydrogen bonds and the energetic stability that they confer have a huge impact on the properties of water.

### **The Boiling Point of Water**

- The boiling point is the temperature when a liquid boils and becomes a gas, usually at normal atmospheric pressure. In the liquid phase, molecules are stuck together, rolling around each other. In the gas phase, molecules break apart from each other and move around in space, each separately. The boiling point is a measure of how much energy we need to separate molecules from each other.
- The two main things that affect the amount of energy needed to separate molecules are the masses of the molecules and the strengths of interactions between the molecules. In general, the heavier the molecule, the more energy—that is, the higher the temperature—we need to boil it.

- Based on this trend, we would expect  $\text{H}_2\text{O}$ , a light molecule, to have a low boiling point. In reality, though, it has a high boiling point of 212 degrees Fahrenheit. This is because of the very strong hydrogen bonding interactions that exist in the water molecule that overwhelm the very low mass of the water molecule and make its boiling point unusually high.
- There's a property related to boiling point that is also unusual for water. For any material, it takes a certain amount of energy to change the phase from solid to liquid, or from liquid to gas. For the liquid-to-gas phase change, this amount of energy is called the heat of vaporization. Because we have to completely break four hydrogen bonds to separate water molecules and make a gas, it takes a fairly large amount of energy to do that, and water has an unusually high heat of vaporization.



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### Ice Floats

- The fact that ice floats on water is very unusual. Most liquids, when they get colder and become solids, sink. But water floats when it becomes ice because of hydrogen bonding. When liquids cool into solids, the individual particles line up into a crystal, a regular arrangement of the particles. Usually, the arrangement of particles in the solid is the structure that has the lowest energy. Also, in most cases, the crystal is denser than the liquid, so it sinks when the solid phase forms.
- In the case of the bent water molecules, the lowest energy occurs when the molecules are pointed so that each water molecule can make four hydrogen bonds, two from the positively charged

hydrogen side of the water molecule and two from the negatively charged oxygen side. So, under normal conditions, a crystal forms, along with a whole lot of empty space.

- In order for the  $\text{H}_2\text{O}$  molecules to align their hydrogen bonds properly and to the lowest-energy arrangement, they have to spread out a bit, causing some emptiness to form between the molecules. When this empty space forms, the volume of the sample increases by about nine percent. When the volume increases, the density decreases, so when the liquid water becomes all solid, the resulting density decreases by about nine percent.
- Basic physics says that less-dense phases float on more-dense phases, so ice floats on water, unlike almost all other substances. About 10 percent of ice floats above the liquid level; the rest is below the surface of the liquid.
- Floating ice was crucial to the development of life on Earth. Most scientists accept the idea that life began in Earth's oceans. In cold areas, if ice would form, because it floats, it would remain at the surface of the oceans, allowing life to continue living beneath it. On the other hand, if ice sank, then the first time it got very cold, ice would start accumulating on the bottom of the ocean, and eventually the ocean would freeze, freezing any life that might be in it.
- Other substances where the solid floats on the liquid include the elements silicon, germanium, and gallium. But water is the only common compound that behaves in such a strange way.

### Water as a Solvent

- Water is one of the best solvents. What makes water such a good solvent is mostly its polarity. Things dissolve in water when water molecules surround the individual particles and separate them from each other. Each dissolved atom or molecule is surrounded by a half-dozen or more water molecules.

- Many things are also polar, or have polar parts—that means that these substances, called solutes, also have partial positive charges and partial negative charges around them. These partial charges attract the ends of the water molecules, and when enough water molecules are attracted, it's more energetically stable for the particles to separate from the solute. It also helps that  $\text{H}_2\text{O}$  is a very small molecule, so it can get into the cracks and crevices that some molecules have.
- Compounds made of charged particles, called ionic compounds, are also soluble in water because the positive and negative ions attract the polar ends of water molecules. Not all ionic compounds are easily dissolved, though. If the charges on the ions are high enough, it takes too much energy to separate them, so they just don't dissolve.
- Despite water's reputation for being a great solvent, it doesn't dissolve everything. For example, oil doesn't dissolve very well, if at all, in water. That's because the oil isn't polar; rather, it's nonpolar. Because oil molecules are nonpolar, there's no energetic stability in surrounding oil molecules with water molecules, and the oil doesn't dissolve.
- Oil does dissolve in liquids that are themselves nonpolar, such as turpentine or gasoline. The idea that polar liquids dissolve polar solutes and nonpolar substances dissolve each other gives us the rule of thumb “like dissolves like”—that is, molecules with similar polarity, or lack thereof, mix together to make solutions. In the case of water, it's such a good solvent because a lot of material around us is polar.

### **The Specific Heat of Water**

- In its most general form, energy is known as heat. When you add heat to an object, it warms up—that is, its temperature increases. Conversely, when you remove heat from an object, it gets colder, and its temperature decreases. The more heat added or removed, the higher or lower the temperature.

- The mass of an object is also a factor. A piece of metal that's twice as massive needs twice as much heat to change its temperature by the same amount. So, the heat added or removed is related to the mass of the object involved and its temperature change.
- The physical property that relates the heat, the mass, and the temperature change of a process is called the specific heat of the material. Specific heat is a physical property of a material, just like density or color or volume. The lower the specific heat, the less heat you need to change the temperature of a material; the higher the specific heat, the more heat you need to change the material's temperature.
- Water has an unusually high specific heat—in fact, it has the second-highest specific heat of any known material, second only to liquid ammonia, but there's not a lot of liquid ammonia around. The high specific heat of water means that it takes a lot of heat energy to warm water up, or cool it down.
- Water's specific heat is very large because of the hydrogen bonds that water molecules are making with each other. When solid or liquid molecules warm up, they shake back and forth faster and faster, until they get so much energy that they change phases into a liquid or a gas. All of this shaking back and forth means that energy needs to overcome the forces that are binding molecules to each other.
- If the binding forces are strong, it takes more heat to overcome them and change the temperature. Water molecules make four hydrogen bonds, each of which is about five percent the strength of a regular chemical bond. It takes a relatively large amount of energy to shake these water molecules back and forth.

- It takes a lot more energy to change the temperature of the oceans than it does the land, and this has major implications for the world's climate. The planet's oceans can both absorb and give off much more heat energy than the land does, and scientists studying the long-term impacts of climate change have to include the huge amount of heat energy that the oceans store.

### Suggested Reading

Silverberg, *Chemistry*, chap. 12.

### Questions to Consider

1. What are some of the different forms and functions of water?
2. How might the physical and chemical properties of water be different if it were a linear molecule, not bent, and therefore weren't polar?

# Matter in Solution

## Lecture 10

**M**ost of the materials around us are solutions. In fact, the air we breathe and the blood in our veins are solutions. As a class of material, solutions have properties that are different from other types of matter, and some of those properties are very useful or desirable. In this lecture, you will learn about solutions. Specifically, you will discover why they form, as well as a few examples of the major impacts they have on our daily lives.

### Mixtures and Solutions

- Fundamentally, matter is either pure or impure. If it's pure, then it's either an element, one of about 90 that are naturally occurring, or it's a compound, one of about 70 million that are currently known. But if it's impure, then technically it's called a mixture.
- An obvious mixture is described as heterogeneous. An example is a mixture of salt and pepper, where it's easy to see what chunk is salt and what chunk is pepper. There are some mixtures, though, that are so intimately mixed that you can't easily tell that it's more than one material, such as salt water. These are called homogeneous mixtures, or solutions.
- Solutions can be all phases of matter. While we usually think of solutions as liquids, there are also solid-phase and gas-phase solutions. Air is a gas-phase solution, while metal alloys are solid solutions.
- The majority component of a solution is called the solvent; it's also the component that has the same phase as the overall solution. The minority component of a solution is called the solute. For a saltwater solution, water is the solvent and salt is the solute.

- Usually, there's only one solvent in a solution, but there can be many solutes. Solvents and solutes can be any phase, and just about any combination of phases is possible, except maybe for liquids or solids dissolved in a gas.
- A cloud, for example, is not a true solution, but a suspension of tiny water droplets suspended in air, and if those droplets become large enough, they fall out of suspension and become rain. We don't see rain in true solutions.
- Any combination of gases is a solution, by the simple definition of a gas. Air is an example of a gas solvent with several gas solutes. Gases can be dissolved in solids or liquids. Soda, beer, and champagne are examples of solutions of carbon dioxide gas dissolved in water, and some metals, such as the element palladium, can absorb hydrogen gas to make a solution.
- Alcohol and water is an example of a liquid-liquid solution; the identities of the solvent and solute depend on how strong the drink is. Examples of a liquid dissolving in a solid are mercury alloys called amalgams, where liquid mercury is dissolved into another solid metal, such as gold or silver. Certain amalgams have been used in the past for dental fillings.

### **Intermolecular Forces in Solutions**

- While science knows that matter is made of atoms and molecules, we also know that atoms and molecules interact with each other, and these interactions strongly influence the properties of matter. The most fundamental force in all atoms and molecules is called the London dispersion force, which is caused by electrons moving around in atoms and molecules.
- As an electron moves, it takes its negative charge along with it. This means that at any point in time, one part of an atom or molecule has a negative charge on one side and, therefore, a leftover positive

charge on the other. Then, in the next instant, the negative charge disappears and shows up on another part of the molecule, in a never-ending dance.

- Because of the constant presence and then absence of negative and positive charges around a molecule, the opposite charges on neighboring molecules are always attracting each other—for a split second. Then, the attraction is gone. Then, it's there again, and then gone.
- The ultimate result is a very weak interaction between molecules that encourages them to stick together—if the temperature is low enough. If the temperature is not low enough, there's enough energy that the substance may be a liquid despite the presence of the dispersion force.
- If the dispersion force is weak and the surrounding temperature provides enough energy, the substance might even be a gas. In fact, this is the basic idea that determines which phase—solid, liquid, or gas—a substance has; it's a balance between the energy provided by temperature and the strength of the intermolecular forces.
- London dispersion forces are weak per electron. As the number of electrons in a molecule increases, usually so does the mass, and definitely so does the London dispersion force.
- If a molecule is shaped so that the atoms are bonded unsymmetrically about its center, then there's going to be an imbalance in the electron distribution in the molecule. Because electrons carry a negative charge, this means that there will be an imbalance in charge around the molecule.
- The molecule will still be electrically neutral overall, but like in the London dispersion forces, there will be sections of the molecule that will have a partial negative charge and sections that will have a partial positive side. However, in this case, instead of being fleeting and short lived, these partial electrical charges are permanent.

- Molecules with such permanent partial charges are called polar; we say that they behave like a dipole. Molecules that don't have these permanent, partially charged regions are called nonpolar. All else being the same, especially mass, polar molecules interact much more strongly with each other than molecules that are nonpolar.
- There's a special type of polar interaction that appears in certain molecules. When a hydrogen atom is covalently bonded to a nitrogen, oxygen, or fluorine atom, the polarity is especially pronounced, and the interactions between molecules are unusually strong. Because of this, the polar interaction between molecules having this type of bond is called hydrogen bonding.
- Molecules that show hydrogen bonding also show significant deviations from expected trends. For example, hydrogen combines with oxygen and sulfur to make very similar compounds,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ .  $\text{H}_2\text{O}$  has half the mass of  $\text{H}_2\text{S}$ , so you would expect it to boil with less energy—that is, at a lower temperature. But  $\text{H}_2\text{O}$  boils at almost 300 degrees higher than  $\text{H}_2\text{S}$ . The lighter molecules need much more energy, a much higher temperature, to boil because of the strong hydrogen bonding interactions between  $\text{H}_2\text{O}$  that  $\text{H}_2\text{S}$  doesn't have.
- Ions are atoms or molecules that have a permanent charge due to loss or gain of one or more electrons. The attraction between positively charged ions, or cations, and negatively charged ions, or anions, is very strong. In fact, it's the strongest force that we see in chemical bonding.
- However, all of the intermolecular interactions that have been introduced are based on electrical charges. If the charges appear and disappear quickly, then the force is relatively weak; if the forces are permanent, or even fully ionic, then the force is relatively strong.

## Energy and Solutions

- How do these intermolecular interactions impact solutions? It's mostly about energy. Most systems of matter want to go to lower energy. At the very least, systems avoid going up in energy, because systems can't make energy from nothing. These ideas control why certain solutions form—and perhaps more importantly, why certain solutions don't form.
- Nonpolar solvents dissolve nonpolar solutes, and polar solvents dissolve polar solutes. This generality is so useful that it has spawned the rule of thumb “like dissolves like,” meaning that solvents having certain intermolecular interactions dissolve solutes that have similar types of intermolecular interactions.
- This is only a rule of thumb—there are some solutions where a nonpolar solvent does dissolve a small amount of a polar solute, or when a polar solvent dissolves a bit of nonpolar solute. But this rule of thumb is very useful in predicting which solutions likely form and which ones don't.
- Knowing this idea, we can engineer some molecules to do what we want. For example, when you change the oil in your car, you might get your hands dirty with a lot of used oil. But when you go over to the sink to wash your hands, the water does nothing—because oil is nonpolar and water is polar. With the soap—sometimes massive quantities of it—you are able to clean your hands. Why?



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**Without soap to dissolve oil, water alone would be ineffective at cleaning your hands.**

- A soap molecule is a very well designed thing. It consists of a long hydrocarbon chain with one ionic end. The long hydrocarbon chain is nonpolar and dissolves in the nonpolar oil. The ionic end is very polar and dissolves in water. With either end dissolved in the different liquids, the soap molecules make it easier to remove the nonpolar oil with water. Without the soap molecule making that bridge, the water would be rather ineffective at cleaning the oil off your hands.

### **Properties of Solutions**

- Most solutions we deal with have only a small amount of solute dissolved in them. We call these solutions dilute. Because they're mostly solvent, these solutions have properties that are very similar to those of the pure solvent. But there are a few differences.
- First, solutions evaporate more slowly than pure solvents, assuming that the solute itself doesn't evaporate. This happens because the solute molecules block solvent molecules from evaporating. However, if the solute does evaporate, then interesting things can happen.
- If the solution is ideal, then the overall solution evaporates at a rate proportional to the composition of the solution. But because of intermolecular interactions, most solutions are not ideal, and the solvent and solute evaporate at different proportions than expected.
- Solutions typically have lower freezing points than the pure solvents. That's because solute particles interfere with the formation of solvent crystals, so it takes lower temperatures to make those crystals—that is, to freeze the solvent.
- There's another property of solutions that seems weird but is actually very important biologically. Imagine two solutions, one concentrated and one dilute, on either side of a very thin membrane. Initially, the two solutions have the same height in the container. Over time, however, the height of the concentrated solution will rise, and the height of the dilute solution will fall and will only stop when the two solutions have the same concentration.

- The difference in the heights of the solutions is called the osmotic pressure, and the process that is occurring is called osmosis. The key to this process is that very thin membrane. It has to be so thin that it allows for movement of solvent molecules from one solution to the other. With solutions of different concentrations, the concentration difference drives the movement of solvent from dilute solution to concentrated solution until both solutions are the same concentration.
- Osmotic pressure is measured in atmospheres, just like gas pressures are measured in atmospheres. One atmosphere is the pressure of our atmosphere at sea level. Osmotic pressures can be substantial, even for dilute solutions.
- One membrane that experiences osmotic pressure effects is a cell wall. Our bodies are constructed from cells that have membranes separating the inside material, largely cytoplasm, from the outside. Concentration differences inside and outside the cell walls set up osmotic pressures that can affect the behavior of the cells and, by extension, the health of a human body.
- Osmotic pressure is the mechanism behind kidney dialysis. If for any reason the kidneys aren't functioning properly, water, waste materials, and minerals build up in the bloodstream, threatening life. Semipermeable membranes are used to transfer excess water and waste out of the bloodstream until other measures, such as a kidney transplant, are possible.
- Osmotic pressure is also one mechanism that trees use to get water from the roots to the leaves, high above our heads. The water isn't defying gravity; it's simply responding to the more concentrated solutions at the leaves and trying to dilute it, giving the tree the water necessary for life.

## Suggested Reading

Silverberg, *Chemistry*, chap. 13.

## Questions to Consider

1. Try to come up with an example of solutions where the solvent is either a liquid or a solid and the solute is either a solid or a liquid or a gas. (Note: There's no such thing as a solid or a liquid solute dissolved in a gas solvent; only gas-gas solutions are recognized by science.)
2. Soap is an example of an emulsifier, a compound that promotes the interactions of polar and nonpolar substances. Emulsifiers are important ingredients in certain foods. Why might this be? Can you think of, or find, some examples of emulsifiers in any foods?

# Interactions: Adhesion and Cohesion

## Lecture 11

**I**ntermolecular interactions are interactions between atoms and molecules. There are several different types of interactions, but they all work at the atomic or molecular level. At the macroscopic level, there are two basic interactions: cohesion, which is a measure of how strongly a sample of matter interacts with itself, and adhesion, which is a measure of how strongly a sample of matter interacts with other substances. In this lecture, you will learn about these two types of attractions. In addition, you will learn about capillary action, as well as types of adhesives.

### Adhesion and Cohesion

- Adhesion and cohesion are ultimately caused by intermolecular interactions, but because we're talking about bulk matter, it's not proper to use "intermolecular" anymore. A material behaves a certain way based on which is stronger, adhesion or cohesion. We always have to consider both types of interactions.
- Water, for example, has fairly strong cohesive forces. In zero gravity, water forms a sphere because the interactions between water molecules are fairly strong. Put a few drops of water into a glass, though, and the water spreads out over the glass. That's because the adhesion between water and glass is stronger than the cohesion within water itself.
- If you take that glass and wax it—like you might wax your car—and then put a few drops of water inside the glass, it beads up into an almost spherical shape. That's because the adhesion between water and wax is much lower than the cohesion within bulk water. This is why we wax our cars: to keep the water from spreading out over the car's surface. Water is necessary for the formation of rust, so by inhibiting the ability of water to wet our metal car, we can slow down the rusting process.

- The element mercury also has strong cohesive forces. Mercury is one of the few elements that is a liquid at room temperature. Mercury stays in small droplets because of the cohesive forces in the liquid. Put some mercury drops in the bottom of a glass, and unlike water, the mercury doesn't cover the bottom of the glass. That's because the adhesive forces between mercury and glass are weaker than the cohesive forces. Mercury only covers the glass when there's enough mercury for gravity to pull it out of its spherical shape.

### **Capillary Action**

- The balance between adhesion and cohesion has some major impacts on our lives that we rarely recognize. Because of adhesion, the water in a glass tends to spread out over the bottom of the glass container. If you fill the container with enough water and look closely, you'd see something interesting. At the interface between the water and the glass, the water actually curves up a bit from the rest of the liquid surface.
- What's happening is caused by adhesion: The water is attracted to the glass so much that it rises ever so slightly up the side of the glass. This rise is called a meniscus. The meniscus effect is seen only next to the glass; the rest of the liquid surface is smooth.
- Imagine that the glass gets narrower and narrower. As it does, the meniscus becomes a larger and larger proportion of the width of the glass. Eventually, it gets to the point where the curvature of the meniscus covers the entire width of the glass, the entire surface of the liquid water. At this point, the glass is called a capillary, which is a very thin tube.
- Something interesting happens to the water in the capillary, though. Because the adhesive force is pulling the edge of the water up a bit, when the capillary is thin enough, the level of the water actually rises up in the tube. This effect is called capillary elevation, one type of behavior generally called capillary action. It has some important consequence in our lives.

- You've seen capillary action if you have ever had your finger pricked as part of a blood test—the blood moving up the tube is capillary action. But you may not realize that you're taking advantage of capillary action when you towel off after a bath, shower, or swim. The towel that you use to dry off is usually a textile composed of tiny fibers that are woven together. The tiny spaces between the fibers act like little capillaries, and as you use the towel to dry off, these capillary spaces suck up the water away from you.
- In part because of capillary action, water gets absorbed into dirt and any other material that is composed of small particles that show adhesion forces for water. This can be problematic for certain building materials, such as brick, concrete, and plaster. If too much water gets absorbed into the building material, problems can occur with the environmental conditions of the building when the weather changes from warm to freezing cold.
- Because water expands when it freezes, if too much water has been absorbed because of capillary action, the building materials can be broken apart or fractured. It's well known in areas that experience snow and ice that roadways and sidewalks suffer damage because of the water absorbed by the pavement. Many drivers have suffered flat tires because of potholes, ultimately caused by ice formed from water absorbed through capillary action.
- Along with osmotic pressure effects, capillary action is primarily responsible for how water gets to the top of plants. Most of the water transported from the roots to the leaves of a plant occurs in a layer of cells called the xylem. The water brings dissolved nutrients with it as well so that photosynthesis can occur in the leaves. After photosynthesis, water with other nutrients returns to the roots through a layer of cells called the phloem.
- While capillary action is important to us and for plant life, there are circumstances when the cohesive forces are larger than the adhesive forces. One example of this is mercury and glass, where

the cohesive forces in mercury are larger than the adhesive forces toward glass. In this case, when mercury is introduced to a capillary, an upside-down meniscus is formed, and the level of the mercury is forced down from its normal surface. This type of capillary action is called capillary depression.

- Although there seems to be no known practical use of capillary depression in nature, humanity uses the general concept in products like water-repellent clothing, which is either made from or coated with materials that have a low adhesion for water. Polyester clothing can be uncomfortable in the summer, ultimately because of capillary depression.

## **Adhesives**

- An adhesive is any substance applied to the surface between two objects with the purpose of keeping those two objects together. It's synonymous with glue or cement. The oldest adhesives were based on tar or plant gums and date back tens of thousands of years.
- Over time, milk proteins and products based on animal proteins, eggs, and beeswax were used. In the 20<sup>th</sup> century, advances in chemistry and the growing availability of petroleum as a source of raw materials allowed for the development of synthetic adhesives, whose properties far surpass natural glues.
- A special type of adhesive is called a mortar, which is a mixture used to hold rocks, stones, or bricks together into some structure. The oldest mortars were clay- and mud-based mixtures, which were used in the earlier Egyptian pyramids. Gypsum and lime mixtures, also known as plaster of Paris, were used in the later pyramids.
- Cement was developed around about 500 B.C.E. in Greece, and today it's the most common mortar. Portland cement is the most common, named after the Isle of Portland, just off the southern coast of England.

- Mortars dry out and become solid, becoming part of the structural support of a building. However, by definition, they are weaker than the components used to construct the building, so that in the event of an accident, it's the mortar that breaks apart instead of the stone or brick. This type of injury to a building or wall is much easier to fix than if the stone or brick itself is broken.
- An adhesive has several advantages over other methods of bonding, such as sewing or mechanical attachment. Perhaps the most important advantage is that it's unnecessary to penetrate the objects with a needle, screw, nail, or other tool in order to join them.
- Dissimilar materials can be joined with adhesives; using adhesives is quick and cost effective, and adhesives can be manufactured to have certain specific properties, such as electrical conductivity. Disadvantages include the fact that many adhesives don't adhere very well at higher temperatures, as well as the need for large surface contact areas for adhesives to perform.
- There are several types of adhesives. Drying adhesives are liquid-based glues that have a solvent that evaporates, and the remaining material forms a hard bond between the objects. Common white glue, used by schoolchildren around the globe, is one example.
- Pressure-sensitive adhesives are the adhesives used for labels, tape, temporary skin connections (such as the sensors used for heart monitors), and sticky notes. You have to apply a little bit of pressure to make your label or tape stick, and the stickiness ranges from easily removable to permanent.
- Hot adhesives, such as the type we find with hot-glue guns, are simply low-melting plastics that can be melted, applied, and then let harden and bond by just cooling down. Many simple home-repair jobs use hot glue, although the bond that hot glue makes isn't very strong.

- There are multipart adhesives, which are typically two liquids that, when mixed together, chemically react to form a solid. Epoxy is a common example of this type of adhesive, as are a variety of resins collectively known as polyurethanes. Some of these types of adhesives use a solvent that needs to evaporate, or dry, before a bond is made.
- If the adhesive doesn't use a solvent, then the chemical reaction that occurs to form the solid is called curing, not drying. These adhesives are fairly strong and are used where strength is needed, such as in the construction of aircraft, cars, boats, and even sporting equipment where high stress is common.
- There are some single-component adhesives that rely on a chemical reaction that is started by heat, or ultraviolet light, or exposure to air or water. Cyanoacrylate glues, or so-called superglues, polymerize in the presence of water to make a strong bond to many materials, including skin. These types of adhesives are useful when quick, strong bonding is needed. They have good tensile strength—that is, glued pieces are hard to pull apart—but have low shear strength, meaning that if you used some to fasten a nut and bolt, you could still unscrew them with reasonable force.
- An adhesive works by one of several methods. A common one is by having the liquid adhesive fill the tiny nooks and crannies that make up a surface, no matter how smooth. When the adhesive hardens, a solid bond is formed.



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**Superglues are useful when quick, strong bonding is needed.**

- Another common mechanism for sticking is the intermolecular forces between molecules at the molecular level. These forces are called van der Waals forces and are quite simply one of the physical properties of the substance. The molecules of the adhesive could be polar or even ionic, meaning that the mechanism of sticking is ultimately the attraction of opposite charges, manifested on the bulk scale.

### Suggested Reading

Silverberg, *Chemistry*, chap. 12.

### Questions to Consider

1. Some adhesives are meant to be used once, while others can be used over and over again. Give some examples of each, and explain how the concepts of adhesion and cohesion apply in each example.
2. What forms of life can walk on a wall? Do intermolecular forces participate in these cases, or is their grip more mechanical?

# Surface Energy: The Interfaces among Us

## Lecture 12

**S**urfaces are all around us—liquid or solid; rough or smooth; painted, varnished, or shellacked. Because they are so ubiquitous, it's difficult to remember that some of them show special properties. Although the surfaces of most solids are constant—indeed, that's partly what defines a solid—surfaces of liquids are flexible, can be changed, and move around. Many liquid surfaces are under the influence of gravity, which determines their shape. In this lecture, you will learn about some of the interesting properties of surfaces.

### Surfaces and Surface Tension

- A surface is a discontinuity, or interface, between one phase of matter and another. We normally think of solids and liquids as having surfaces, but not gases. We can talk about the surface of a gas, but that situation is trickier than talking about the surface of the other two, so-called condensed phases.
- In a glass of liquid water, the molecules of water are all interacting with each other. If you're thinking of a molecule of water in the middle of the glass, then those interactions are going on all around the molecule: top, bottom, left, right, and sides.
- For a water molecule that's at the surface, there are interactions left, right, side, and underneath—but not on top, because there aren't any water molecules on top, because you're at the surface. Because of this, there is an imbalance of forces on the molecules at the surface, leading to a sort of tension at the surface. This is called surface tension. In general, the stronger the intermolecular forces, the stronger the surface tension.
- Surface tension can impact the bulk properties of the liquid, even though it's a property of the surface. Because surface tension has units of energy per unit area, surface tension is also referred

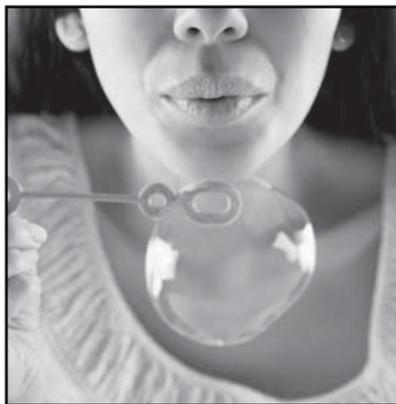
to as surface energy. Objects tend to go to states of minimum energy, so in some circumstances, a liquid will try to minimize its surface area.

- A sphere is the shape that contains the most volume with the lowest surface area, so if no other forces act on a liquid, it tends to form a sphere. Small drops of water look like spheres, as do droplets of mercury. A larger sample of water in zero gravity, like in a space station, will also take on a spherical shape. However, anything but the smallest droplets of liquid flatten out because of gravity.

### **Films, Bubbles, and Droplets**

- Because surface tension is also known as surface energy, there are some energy considerations about surfaces. It takes energy to increase the surface area of a surface, and surfaces tend to decrease their surface area as much as they can. One way to demonstrate this is to consider a circumstance where there are two parallel surfaces very close together—that is, a film.
- One kind of film that's very easy to play with is a soap film. A rectangular soap film tries to adopt a minimum area. In a rigid frame, the soap film stays stretched out flat, because any bend would increase its surface area and its surface energy. If one part of the frame moves easily, then it will move to decrease the surface energy by decreasing the surface area.
- Films can also be made when two liquids don't dissolve each other, but do wet each other to some degree. When two liquids don't dissolve in each other, they are called immiscible. Water and oil are examples of two liquids that are immiscible.
- Thin films can be used for intentional purposes; when they are, they're called coatings. One example is the thin coating of epoxy inside most food and beverage cans to keep the food from reacting with the metal can. Sometimes films are used intentionally for their optical properties, as they are with antireflection and ultraviolet-protecting coatings on sunglasses for better and safer vision.

- Soap films make bubbles—not just bubbles in your kitchen or bathroom sink, but bubbles that you blow with a little plastic wand. Individual bubbles are always spherical, because the sphere is the shape that has the lowest surface area, and surface tension—surface energy—encourages liquids to minimize their area.



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**Individual bubbles are spherical because that is the shape with the lowest surface area.**

- Bubbles are usually very thin films, but what happens if the bubble's film gets thicker and thicker? Eventually, we get to the center of the bubble and we have a droplet. Curiously, the pressure inside the droplet is higher than the pressure outside the droplet, which has some interesting effects on evaporation.
- The smaller the size, the larger the pressure difference. This means that the smaller the droplet, the more pressure there is to drive liquid molecules into the gas phase—that is, smaller droplets evaporate faster than large droplets. This idea has implications for issues as diverse as spraying on perfume and cologne to supplying gasoline to a car's engine.

### **Wetting and Surfactants**

- If the attraction between a liquid and a solid surface is stronger than the attraction within the liquid itself, then the liquid will spread out on the surface. This is called wetting. One way to express wetting is to measure the angle between the edge of the droplet and the solid, called the contact angle. If the angle is less than 90 degrees, we say that the liquid wets the surface. If the angle is greater than 90 degrees, then the liquid does not wet the surface.

- A liquid that wets a solid also shows capillary action. A capillary is simply a very thin tube. If a liquid is attracted to the tube itself, like water is attracted to glass, then it gets sucked up the capillary. However, after reaching a certain height, gravity takes over, and the rise up the tube stops.
- Because surface tension is really a surface energy and it takes energy to rise up against gravity, the amount that a liquid rises in a capillary can be used to measure the surface tension of a liquid.
- Wetting is favored when the liquid has a low surface tension. That's because surface tension is actually surface energy, and when such a liquid spreads out, the energy of the new surface is lower.
- Water, the most common liquid around us, has one of the highest surface tensions of any pure liquid—more than three times that of rubbing alcohol. It's because of the strong interactions between water molecules that it has such a high surface tension. In washing machines, the better that water wets the clothes, the better it can clean them. But if water has such a high surface tension, there might be limits to how well we can use water for washing.
- Both soaps and detergents have a polar, or hydrophilic, end that interacts well with polar water molecules and a nonpolar, or hydrophobic, end that doesn't interact well with water molecules. Because of this, the soap or detergent molecules tend to concentrate themselves near the liquid water's surface, and in doing so, they disrupt the interactions between water molecules.



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**Soaps and detergents are substances that have the property of, among other things, lowering the surface tension of its solution in water, making the water more wettable.**

- Because these strong interactions between water molecules are the root cause of surface tension, by disrupting them, soaps and detergents decrease the surface tension of the water, allowing the water to wash clothes, dishes, and hands better. The molecules also help dissolve grease and oils because their hydrophobic ends are more soluble in grease and oil.
- A molecule that affects the surface properties of a solvent like this is called a surfactant, a contraction of “surface” and “reactant.” Surfactants can be used as emulsifiers, which keep two or more liquid phases from separating, like the oil and vinegar in salad dressings. Surfactants can also act as foaming agents, because lowering the surface tension makes it easier to make all the tiny bubbles in a foam.
- One interesting medical use of surfactants is for premature babies. If the baby is too premature, his or her lungs aren’t fully developed yet. Doctors will spray a surfactant into the baby’s lungs. The surfactant lowers the surface tension of the alveoli, the tiny sacs in the lungs where oxygen and carbon dioxide exchange with the bloodstream. This allows the alveoli to expand and contract more easily, allowing the baby to breathe easier.

### **Solid Surfaces**

- A surface that’s smooth to the touch may not actually be smooth at the atomic level. Our sense of touch is limited to about one micron, or half of a thousandth of an inch, under ideal conditions, meaning that any irregularity smaller than that is undetectable to us. But at the atomic scale, one micron is still very rough; it is the equivalent of about 5,000 atoms.
- Not only are surfaces very rough, but they’re also dirty. For example, if a surface is exposed to air at normal pressure, then what we think of as a solid surface is actually being bombarded with molecules of nitrogen, oxygen, water vapor, carbon dioxide, and argon gases. Any pollutants that might be in the air are also hitting the surface.

- It's estimated that at normal atmospheric pressure, if every air molecule were to stick to a surface when it hits, we would build up a layer of about six inches per second. So, it's pretty clear that a lot of those molecules are simply bouncing off the surface, but some of the molecules are sticking, making the surface rather dirty at the atomic scale.
- We say that the molecules are adsorbed onto the surface. In some cases, actual chemical reactions can occur. For example, if hydrogen sulfide gas gets adsorbed onto a silver metal surface, it can react to make silver sulfide, which we call tarnish.
- Scientists and engineers can make surfaces that are atomically smooth—or practically so. They have to do it under conditions of very high vacuum, but this can be done rather routinely. On such smooth surfaces, the atoms or molecules are lined up precisely, making a sort of two-dimensional crystal of atomic particles.
- At the atomic level, the organization of the atoms depends on the angle of the surface cutting into the bulk. For example, a nicely cut diamond has surfaces at all sorts of angles to make it sparkle brilliantly. But because these surfaces are at all different angles, the arrangements of carbon atoms are all different as well, even if each surface is atomically smooth. The atoms are at different distances from each other and make angles that can be different, from surface to surface.
- Certain surfaces can affect chemical reactions by speeding them up. A substance that does this is called a catalyst. Catalysts are very important in our society: They promote desirable chemical processes to save us money, allow us to synthesize more valuable products, and even reduce pollution from our cars.
- The problem is that not every surface is a catalyst. Only certain elements or compounds behave like catalysts. More importantly, in some cases, only certain surfaces with certain arrangements of atoms at the surface will be a catalyst—and only for certain chemical

reactions. The exact angle of the surface gives arrangements of atoms that can be different, and these surfaces have different chemical and physical properties.

- There's some exciting artistic work happening on atomically clean surfaces. Using an ultrafine metal needle, scientists have been able to move individual atoms around and place them at specific points on the surface.
- In 1990, researchers at IBM were able to move atoms around on an atomically flat surface and were able to spell out the letters "I," "B," and "M." In 1999, scientists were able to move individual iron atoms around on a copper surface to spell out the Japanese word for atom, as well as individual carbon monoxide molecules into the shape of a stick-figured person.
- This suggests that technology has gotten to the point that we can assemble any molecule we want to on a surface, one atom at a time. We're not exactly there yet; scientists who work with surfaces have only started scratching the surface of using these surfaces as canvasses for their artwork. Still, the potential is there, and it's exciting to think of what will emerge.

### Suggested Reading

Somorjai, *Chemistry in Two Dimensions*.

### Questions to Consider

1. Why do you think droplets of water bead up after you wax your car?
2. What shape would the surface of a bubble take if a cubical or pyramidal wire form were dunked into soapy water? Perhaps you can find out by doing it yourself.

# The Eloquent Chemistry of Carbon Compounds

## Lecture 13

The science of chemistry can be separated into two parts: inorganic chemistry and organic chemistry. Inorganic chemistry is the study of all of the elements in the periodic table except for carbon; organic chemistry is the study of the chemistry of carbon. Carbon demonstrates the widest variety of chemistry of any element known. Carbon forms more compounds, more types of compounds, than any other element. In fact, carbon compounds are the basis of life. In this lecture, you will discover the many reasons why carbon deserves a field of chemistry all to itself.

### Hydrocarbons

- The simplest organic compounds are called hydrocarbons, which are compounds that contain only the elements carbon and hydrogen. If all of the bonds in the hydrocarbon are single covalent bonds, the hydrocarbons are called alkanes.
- Methane, whose chemical formula is  $\text{CH}_4$  and which is the principal component of natural gas, is the simplest alkane. The next-simplest alkane is ethane, whose formula is  $\text{C}_2\text{H}_6$  and has the two carbon atoms bonded together. Then, there's propane,  $\text{C}_3\text{H}_8$ , which has the three carbon atoms linked together and is used to fuel some of our barbecue grills. Then, there's butane,  $\text{C}_4\text{H}_{10}$ , a four-carbon chain surrounded by hydrogen atoms that is used in lighters.
- These compounds consist of a chain of carbon atoms surrounded by hydrogen atoms—that's one type of hydrocarbon, and it illustrates one of the reasons carbon is central to organic chemistry: It makes long chains of molecules. Some alkanes have chains that have dozens, hundreds, or even thousands of carbon atoms, all linked one after another.

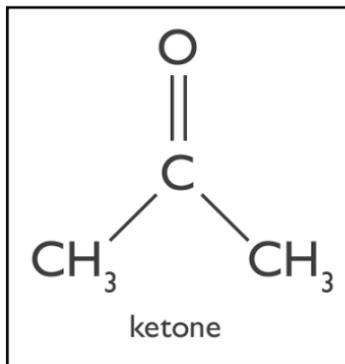
- But it doesn't have to be a straight chain. At any carbon atom in a chain, more than one carbon atom can be bonded and the chain can go off into two, or even three, other directions. These are called branched alkanes, and they only add to the complexity of possible hydrocarbons.
- As simple as they are, alkanes are very important in our society. In addition to methane, propane, and butane, gasoline is mostly hydrocarbons. We use alkanes largely for fuels—to cook our food, heat our houses, and power our vehicles.

### **Functional Groups**

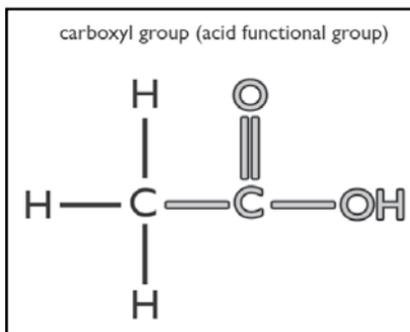
- If organic chemicals were nothing but hydrocarbons, then organic chemistry would be rather boring. The real excitement in organic chemicals is the fact that carbon makes chemical bonds with other elements, or even itself, in different ways, leading to a huge variety in chemical and physical properties.
- A certain bonding of atoms or elements that leads to a certain set of chemical properties in a molecule is called a functional group. It's called that because it strongly influences the way a molecule functions, if it has this certain bonding arrangement. The existence of a large number of functional groups is largely responsible for the huge variety and complexity of organic compounds.
- Perhaps the simplest functional group is when two bonds exist between adjacent carbon atoms in a chain; this is called a double bond. A carbon-carbon double bond undergoes certain chemical reactions that carbon-carbon single bonds don't, which is what makes it a functional group, called the alkene functional group.
- Some molecules also have three bonds between adjacent carbon atoms, which is called a carbon-carbon triple bond. A triple bond is also considered a functional group; it's called an alkyne. Alkenes and alkynes are also hydrocarbons, just like alkanes.

- Most functional groups, though, involve atoms other than carbon and hydrogen. In organic chemistry, such atoms are called heteroatoms. For example, one heteroatom could be a chlorine atom substituting for a hydrogen atom in an alkane.
- Many compounds, especially simple ones, were well known before a good understanding of their nature was understood. Because of this, many of these simple compounds were given common names. Over time, once our understanding of organic chemicals grew, we realized that a systematic naming system was necessary. Learning this system of naming is an important part of every chemist's education.
- In the chlorine example of a functional group, a heteroatom simply replaces a hydrogen atom in an organic molecule. There are other functional groups, though, that are specific groupings of atoms, not just replacements.
- For example, when an oxygen atom and a hydrogen atom are bonded together, we have something called the alcohol functional group. Because an oxygen atom usually makes two bonds, the alcohol functional group can be connected to an organic molecule in place of a hydrogen atom. When we do this, we make an organic molecule called an alcohol.
- Ethyl alcohol, or ethanol, is a common drink. It turns out, though, that ethyl alcohol isn't the simplest alcohol. The simplest alcohol is methyl alcohol, a compound made by taking methane, the one-carbon hydrocarbon, and adding an alcohol functional group to it. Methanol, as it's also called, should not be drunk, because the body treats it as a poison—first you go blind, and then you die.
- Ethyl alcohol is an alcohol that comes from ethane, the two-carbon hydrocarbon. When drunk in moderation, ethyl alcohol can be inebriating, but drinking too much ethyl alcohol in a short period of time can be toxic.

- The names methanol and ethanol, the formal names for these two alcohols, end in the suffix “-ol.” This is a standard organic chemistry naming tool to indicate an alcohol functional group in a molecule. In fact, cholesterol has an alcohol functional group, too.
- If, instead of having a hydrogen atom on one bond, you have a carbon-containing group making both bonds to the oxygen atom, you have a functional group called an ether. The compound that was once used as an anesthetic, diethyl ether, is one example of this type of compound. Like chloroform, it’s rarely used as an anesthetic anymore, but for a different reason: Ether is highly flammable, and its vapors can explode if they build up too much.
- Oxygen makes other functional groups. The oxygen atom typically makes two bonds, and if both of those bonds are made to a single carbon atom—that is, if we have a double bond between a carbon atom and an oxygen atom—then we have a functional group called a carbonyl group.
- Because carbon atoms tend to make four bonds, there are still two more bonds that the carbon atom can make. If at least one of these additional bonds is to a hydrogen atom, then we have an aldehyde functional group. If the other bond is also made to a hydrogen atom, then we have a compound called formaldehyde, which is probably best known as a preservative of biological samples.
- But if both of the other two bonds on the carbon in the carbonyl group are made to carbon atoms, then the functional group is called a ketone. The compound acetone, which has three carbon atoms, is the simplest ketone. It’s a liquid at room temperature and is a pretty good solvent, which is why it is used as nail polish remover.

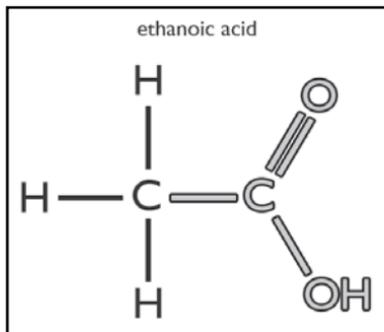


- If you take this carbonyl functional group and attach an alcohol functional group to the carbon, then you've made something called the carboxyl group or, in more common terms, the acid functional group. Although organic acids behave chemically like acids, they're all rather weak acids. In fact, we regularly eat and drink several organic acids, including citric acid, found in oranges, lemons, and limes.



- The organic acid functional group has one more bond to make to the carbon atom, and if that bond is made to a hydrogen atom, then we have the compound whose common name is formic acid. Because formic acid has a single carbon atom in it, its formal name comes from the word “methane,” and it’s known as methanoic acid.

- The next-largest organic acid has two carbon atoms in it, and its name comes from “ethane,” the two-carbon hydrocarbon. Formally, we call it ethanoic acid, but its common name is acetic acid, which is the acid in vinegar.



- For oxygen, if you take the acid functional group and replace the hydrogen atom with a carbon-containing group, then you've made a functional group called an ester. Esters are very interesting compounds because many of them have rather nice tastes and odors. In fact, many esters are used as additives in commercial products to give them a particular flavor or aroma, including perfumes and colognes.



- Nitrogen makes other functional groups, such as one with oxygen having the formula  $\text{NO}_2$ , which is called the nitro functional group and is found in explosives like nitroglycerine and trinitrotoluene (TNT). Other heteroatoms show up, too; sulfur and phosphorus are two other common elements in functional groups.
- Functional groups of heteroatoms may also contain hydrogen or oxygen, or they may include double or triple bonds. It's this wide variety of functional groups that adds complexity to organic molecules. Also, many molecules contain more than one functional group, making things even more complex.
- One very important group of organic chemicals is the amino acids, which are the building blocks of proteins. Amino acids have at least two functional groups: an amine functional group and an acid functional group. One amino acid is glutamine, a form of which is part of monosodium glutamate, a common food additive. The glutamine molecule has four different functional groups—and this is a relatively small molecule in organic chemistry.

### Three-Dimensional Structure

- Carbon can make up to four bonds to up to four different atoms. Those four bonds don't make a square, as some might suspect; rather, they point toward the corner of a tetrahedron, a three-dimensional arrangement. When carbon makes a double bond or a triple bond to another atom, it loses its tetrahedral geometry, but anytime a carbon atom makes bonds to four other atoms, the geometry around this carbon atom is roughly tetrahedral.
- If there are four different atoms or groups connected to that central carbon atom, then there are two different ways that these four groups can be bonded three-dimensionally. It's very much like your left and right hands: Your two hands are mirror images of each other, yet no movement or rotation will ever make it so that your left hand and your right hand are exactly superimposed in three-dimensional space. This only works when the carbon atom is bonded to four different groups.

- This property of three-dimensional molecules is called chirality, a word that comes from the Greek word for hand. Two different molecules that are exactly the same except that they are not superimposable on each other are called enantiomers of each other. Individually, these molecules have exactly the same chemical and physical properties; they are just mirror images of each other.
- The situation changes when a molecule has more than one carbon atom that has four different bonds. In this case, there are more than two possible three-dimensional shapes a molecule can have, and when this is the case, physical and chemical properties can be different.
- If a molecule has  $x$  carbon atoms with four different groups, then there are  $2^x$  different possible three-dimensional structures, and only one of those structures might be important, especially in biological systems. With larger molecules, there are larger numbers of chiral carbons, and complexity increases exponentially.

### Suggested Reading

Bruice, *Organic Chemistry*.

### Questions to Consider

1. Based on past experience, can you think of other substances whose names have “acid” in them that are probably organic acids?
2. Using a pencil and a paper, can you draw all of the possible ways that seven carbon atoms can bond together to make different molecules? (Hint: There are nine of them.)

# Materials for Body Implants

## Lecture 14

**T**he human body is a bunch of biochemical reactions and structural mechanisms that keep on going for sometimes more than 100 years. For most of us, much of the time these biochemical reactions and structural components work fine. Every once in while, however, something doesn't work right, and our bodies break down. As you will learn in this lecture, our knowledge of materials and their biochemistry has allowed us to develop replacement body parts that we can implant into the human body, increasing both the length and the quality of our lives.

### The Human Body

- The human body is a pretty hostile place. For example, the stomach is full of hydrochloric acid—obviously a chemically hazardous spot. But food starts breaking down almost immediately, because our saliva contains enzymes that start reacting with our food even as we chew. As we go further down the digestive tract, we see that our body tissues are constantly being exposed to the body's waste products without being harmed.
- Not only does the bloodstream have enzymes, but it also has antibodies that attack bacteria and viruses as part of our immune system. If all goes well, these antibodies destroy invading germs so that they don't make us sick. In most cases, the immune system only fights off invaders, but there are some diseases called autoimmune diseases where the immune system starts fighting the body itself, including celiac disease and type 1 diabetes.
- The element chlorine is present in the human body at a concentration of about two parts per thousand. However, it's never present in the elemental form of chlorine—that would be poisonous. Rather, it's present in the form of the negatively charged

chloride ion. The problem with the chloride ion is that it's known to promote corrosion in many metals, including stainless steel and many high-tech alloys.

- This means that we're going to have to be careful if we want to use certain metals as replacement body parts; if they corrode, they may not provide long-term structural support, or may even poison a person as they dissolve inside their body.
- With all of these things to watch out for, there are four main considerations when evaluating a material for its use as an implant.
  - It must be able to withstand the environment of the human body, including a temperature of 98.6 degrees Fahrenheit and the possible acidic, corrosive, enzymatic conditions.
  - It must invoke minimal response by the body's immune system, which has evolved to attack foreign material in the body. Adverse immune responses can be treated with drug therapy, but if drugs are not needed, so much the better. On a related note, the material must itself be nontoxic to the body, and must not promote diseases.
  - It must be structurally able to perform its job if providing structural support is necessary.
  - It should be cost effective, although depending on the need, this is less important.
- Not every implant addresses these four concerns equally well, but for implants that are used, most of these requirements can be met.

### **Teeth Replacements**

- One of the oldest body parts to be replaced with implants is the tooth. Sometimes a small part of the tooth is replaced because it's been worn away or a cavity forms; in other cases, the entire tooth is replaced by some other material.

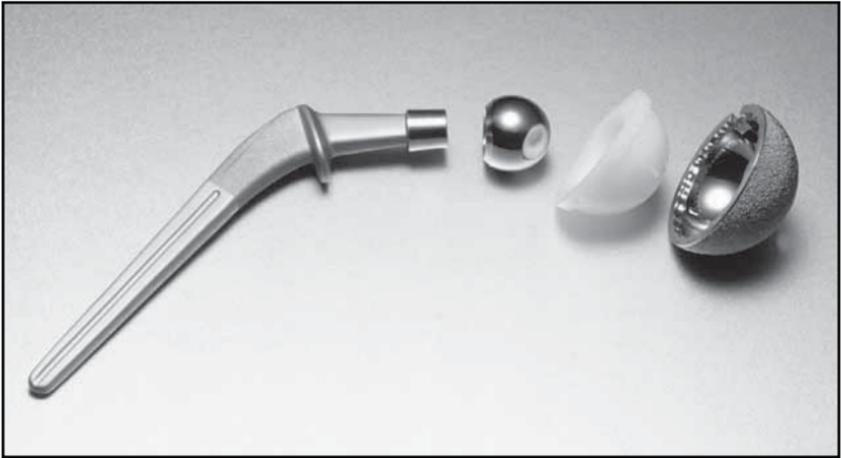
- Dental restorations of any sort are a tricky type of implant because of the extreme environment of the mouth and the severe pressures put on the teeth by chewing. The mouth is warm, wet, full of enzymes, and ever so slightly acidic. It's not too acidic; otherwise, our teeth would slowly dissolve.
- But what we put in our mouth can be even more reactive, including acids from foods like fruits, fibrous tissues from plants and meats, hot coffee, and cold ice cream. Our teeth are directly exposed to a wide range of conditions. Any material we use to repair or replace teeth has to be up to the challenge.
- Many people get cavities in their teeth even if they practice the best dental hygiene. Historically, one of the first materials used to fill small holes in our teeth was dental amalgam. An amalgam is an alloy that contains mercury. The amalgam—which is 50 percent mercury, about 25 percent silver, and some tin, copper, and a few other metals—is easy to work with, hardens into a tough solid, and is resistant to the harsh conditions of the mouth. It's still widely used around the world.
- Another material used for fillings is called dental composite, which is essentially a resin, or plastic, with finely ground sand mixed in to give it a white appearance, similar to teeth. Most composites don't have the longevity that dental amalgams do, but the fact that they have the same color as teeth make some people prefer them from a cosmetic perspective.
- For restoration of larger portions of a tooth, materials like porcelain, a type of ceramic, are used. These porcelains are typically made of aluminum oxide or zirconium oxide that are fused together at high temperature. Dentists can make a mold of the remaining tooth and fashion a replacement section that is then bonded to the leftover bone.

- Gold and silver alloys are also used to replace parts of teeth. By themselves, pure gold and pure silver are rather soft and would be poor tooth replacements. Instead, alloys are used that contain as much as 80 percent to as little as 40 percent of the base metal because they have superior mechanical behavior.
- If an entire tooth needs to be replaced, the actual tooth itself is usually ceramic, although it can be a noble metal like gold or silver. Mounting it into the jaw is another issue. Usually, titanium implants are screwed into the jaw, with the artificial tooth mounted onto the end of the implant.
- Titanium, either pure or alloyed with other metals, is one of the few metals that does not react badly in the body and, therefore, is very biocompatible. It's also relatively light and strong, so it's well suited for dental uses. Once a titanium implant is screwed into the jaw and the bone fuses around the screw, an artificial ceramic tooth can be mounted onto the end, and no one but your dentist will know the difference.
- Dentures are used to replace multiple teeth. Generally, dentures are removable instead of being permanently implanted. They can be partial, which replaces a few adjacent teeth, or full, which replaces the entire top or bottom, each of which is called an arch.

### **Bone Replacements**

- Historically, stainless steel has been used to replace bones, but some people are sensitive to some of the metals in the various stainless steel alloys. Today, titanium is the material of choice for bone replacements, just like for dental implants. It's half as heavy as steel, is very resistant to corrosion, and has excellent mechanical properties. Instead of pure titanium, an alloy with about five percent each of aluminum and vanadium or niobium is used; these minor components provide additional strength to the metal.

- To better match the mechanical properties of actual bone, the implant can be made porous rather than completely solid. Instead of being a solid piece of metal, metal powder is heated until the powder particles just begin to fuse together.
- In order to bond better with any remaining bone, sometimes the titanium implant will be coated with hydroxyapatite, which is the scientific name for the mineral portion of bone. Hydroxyapatite is a mineral containing calcium, phosphorus, oxygen, and hydrogen.
- Because titanium is very biocompatible, it's one of the materials of choice for long-term implants because it doesn't chemically react in the body. It also has the advantage of being nonmagnetic, so people can get magnetic resonance imaging (MRIs) without problems associated with magnetic metals.
- These advantages also make titanium alloys the preferable material for small screws, plates, or rods that might need to be implanted to provide additional structure or strength after injuries or surgeries. However, titanium will still set off metal detectors.
- Sometimes a joint, not just a bone, needs to be replaced. One of the more common joint replacements is at the hip, where the issue is not just structural but also functional. In this case, there are two approaches: the hard-on-hard and hard-on-soft approaches. For the hard-on-hard approach, either chrome alloys or ceramics are fashioned into a replacement ball-and-socket joint. For the hard-on-soft approach, a metal or ceramic ball is polished as finely as possible, and then an ultra-high-molecular-weight polyethylene plastic is used as the socket.
- The bones are connected by several thick fibers called ligaments, and the surfaces of the bones are covered with a thick, tough tissue called articular cartilage. In some people, this cartilage can wear out over time, leading to pain and swelling. Doctors can replace this worn-out cartilage layer with pads of silicone that will allow the joint to slide back and forth again.



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One of the more common joint replacements is at the hip, where the issue is not just structural but also functional.

- Silicones are mixed silicon-oxygen-organic group polymers. The properties of the silicone depend on the identity or identities of the carbon-containing groups on the chain. Because of their variable properties, the right silicone can be used for joint replacement, depending on the demands of the joint.

### Breast Implants

- Breast implants can be used as part of reconstructive surgery, either following mastectomies or deformities, or for cosmetic purposes. Early breast implants were not very successful and included materials like a patient's own fat tissue, paraffin wax, glass or rubber inserts, and plastic sponges. Modern, safe implants were developed in the 1960s and are either a saline-filled silicone sac or a silicone-filled silicone sac.
- There are several surgical methods for inserting a breast implant, but they all require making an incision and placing the implant in the chest. When using a saline implant, a smaller incision can be made because the implant is not filled with saline until after it's been implanted.

- The saline that's used is a 0.90 percent solution of sodium chloride—table salt—in sterile water. This type of solution is called normal saline and has the same approximate salt concentration as blood. When using a silicone-filled implant, a larger incision must be made because the implant is already filled with silicone.
- Different silicones have widely different physical properties, and the silicones used to fill breast implants have properties that provide the appropriate physical and visual effect. Most of them are either thick liquids or are a bit gelatinous. Because the silicone sac is biologically inert, the body's immune defenses aren't activated for either type of implant.
- One of the biggest potential problems with breast implants is possible leakage of the saline or silicone from a broken sac, which eventually completely deflates. A breast implant is a foreign object in the body, and in some cases, the body can react to it by surrounding the implant with scar tissue to isolate it. Optional breast implants need to be seriously considered and not taken lightly.

### Stents

- The human body is full of tubes. For example, arteries and veins are just biological tubes that transport blood. The kidney passes waste liquids through tubes, and we eat and breathe through tubes. Sometimes, because of disease or injury, some of these tubes collapse, and that can be hazardous to our health. There are implants, however, that help keep biological tubes open. They're called stents.
- Most people know stents through their use in arteries, especially coronary arteries that supply the heart with blood. The stent is a wire mesh tube that is usually made out of stainless steel or an alloy of chromium and cobalt.

- The insertion of a coronary stent is called angioplasty, and it involves the insertion of a catheter with a tiny balloon on one end into the circulatory system, usually through the femoral artery in the leg. The stent is wrapped around the balloon, which is initially deflated.
- Using X-ray visualization, the doctor pushes the catheter through the circulatory system until the balloon reaches the proper blocked artery, and then the doctor inflates the balloon. As the balloon expands, so does the stent, until the stent is firmly pushing against the collapsing artery. The doctor then removes the catheter, and the procedure is done. It's important that the stent be firmly against the artery wall; otherwise, it can act as a site for blood clot formation.

### Suggested Reading

Williams, *Williams Dictionary of Biomaterials*.

### Questions to Consider

1. Given that there are four main requirements when evaluating a material for a body implant, how would you rank them, from most important to least important?
2. From what you know about the human body, do you think that there are some parts that could never be replaced by an implant?

# The Chemistry of Food and Drink

## Lecture 15

**E**ating and drinking are the ways we fuel ourselves for everyday life. In addition to providing us with the raw materials we need to grow and replenish our bodies, food provides us with the energy we need for our cells, muscles, and organs to work. A large part of what we drink is just a tasteless, odorless, colorless liquid, but mostly everything we eat comes from living things, either plant or animal. In this lecture, you will learn about the materials we eat—specifically, for breakfast.

### Orange Juice

- Orange juice comes from squeezed oranges, and it is pretty acidic—about  $1/100^{\text{th}}$  as acidic as stomach acid. Its acidity comes from a compound called citric acid. Citrus fruits are very fragrant, can be very sour tasting because of the presence of acid, and are rather juicy.
- Citrus fruits also contain a healthy amount of vitamin C. Vitamin C is very important biochemically, especially in the production of connective tissue. Most forms of life can synthesize vitamin C themselves, but humans cannot and must get it from their diet.
- Eating fruits and vegetables has long been recognized as healthy, but sometimes they're not readily available. In some circumstances, people became afflicted with a disease called scurvy. Although known since ancient times, it became rampant with the development of long-term sea voyages. Eventually, it was found that eating citrus fruits or drinking citrus juice, because of their vitamin C content, prevented scurvy.



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**As evidence for vitamins was discovered, they were given letters of the alphabet in order; vitamin C was the third one investigated.**

## Eggs

- Eggs are one of the most versatile foods. Most of the eggs eaten in the United States are chicken eggs, but we also eat the eggs of ducks, quail, goose, fish, and even ostrich.
- An egg has an interesting structure. From our perspective, we usually simplify the egg into three parts: a shell, the white, and the yolk. Chemically, the shell is almost pure calcium carbonate, with a bit of protein mixed in to keep the shell from getting too brittle. Because of the spheroidal shape of the shell, it's fairly strong, so it can protect the growing embryo inside.
- The color of the eggshell has nothing to do with what's inside the egg; it's solely determined by the species of bird that lays the egg. Contrary to some beliefs, brown eggs are no more or less nutritious than white eggs or green eggs or blue eggs.
- Inside the egg, what we call the white of the egg is actually a clear liquid material that is 90 percent water and 10 percent proteins, mostly a protein called albumin. The job of the white in the egg is to cushion the yolk. The egg white contains virtually no fat.
- Unlike orange juice, egg whites are slightly alkaline. At a temperature of 143 degrees Fahrenheit, the egg white starts to coagulate, or denature. Denaturing is the process in which proteins lose their structure, usually due to heat or chemicals. When the proteins lose their original structure, they can cross-link and form a solid mass, trapping the water inside—and then it turns white. For egg proteins, this process is irreversible. Cooking the white until it's hard makes the protein more digestible and kills some, but not all, microorganisms.



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**Yolks denature at higher temperatures than the whites, making sunny-side up eggs possible.**

- The yolk of the egg is the food source of the embryo, if the egg were ever fertilized. It contains vitamins, minerals, proteins, fat, and cholesterol to support a growing animal inside the egg. The yellow color comes from pigments called xanthophylls that are present in the chicken's diet and have little nutritional value. Chickens with different diets can have radically differently colored yolks, but the nutritional difference is negligible.
- When cooking, the yolk starts to denature at 148 degrees Fahrenheit, a slightly higher temperature than the white. This is why we can have sunny-side up eggs with a solid white and a runny yolk.

### Bread and Toast

- Most of the breads we eat for breakfast are yeast breads, which use yeast as a rising, or leavening, agent. Yeast are fungi that can live without the Sun. There are many different kinds of yeast, and the species of yeast used in cooking converts carbohydrates into carbon dioxide and alcohol in a process known as fermentation.
- Yeast can metabolize carbohydrates either aerobically—that is, with oxygen—or anaerobically—without oxygen. In the presence of oxygen, the overall chemical reaction that the yeast undergo is the same as the combustion of glucose: Glucose and oxygen react to make carbon dioxide and water:  $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ .
- This is the initial reaction that occurs as the yeast in bread dough starts working to produce carbon dioxide gas to puff up, or leaven, the dough.
- When oxygen runs out, the overall chemical reaction is a bit different: A glucose molecule is converted by the yeast into carbon dioxide and ethyl alcohol, or ethanol:  $C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$ .
- This is the second reaction that occurs as yeast works to leaven the dough with the carbon dioxide that has formed. Alcohol is produced, but very little, and it evaporates upon baking.

- Not all breads rise because of yeast action. A bread formed using some leavening agent other than yeast is called a quick bread. Most quick breads use some sort of chemical reaction that generates carbon dioxide gas. Usually, this entails using some carbonate compound and reacting it with some weak acid, such as citric acid, tartaric acid, or the acids in buttermilk. The reaction of the carbonate and the acid yields carbon dioxide. A few common carbonate compounds are sodium bicarbonate (baking soda) and baking powder.
- Toasting bread for your breakfast is an interesting chemical process. While many foods turn dark and eventually burn when exposed to high heat, certain foods experience a so-called browning reaction that occurs prior to burning. In these cases, the amino acids from proteins in the food react with sugar molecules to make brown, and occasionally flavorful, products. The reaction between amino acids and sugars is called the Maillard reaction, and it occurs not only in breads but in meats as well.

## **Bacon**

- Bacon can come from many parts of a pig, but in the United States, it's almost exclusively from the pork belly. First, the pork belly is cured, which means that it's soaked in saltwater, called a brine, or packed with salt; this is a means of preserving the meat for long-term storage. Other ingredients—such as nitrates, nitrites, or sugar—can be used in curing to add other flavors. Then, it can be smoked, which gives even more flavors to the meat.
- The use of nitrates and nitrites in the curing of bacon is a bit controversial. When these compounds interact with proteins at high temperatures, such as those found in cooking, new compounds called nitrosamines are formed. Nitrosamines are known to cause cancer in laboratory animals, so some people have argued for the removal of nitrates and nitrites in the curing process. However, they do decrease the chance of botulism, so instead of removing nitrates and nitrites, many countries regulate the amount that can be used.

## Milk

- Milk is a liquid secreted by the mammary glands of mammals that is used to feed their young, as many human mothers do. The secretion of milk is one of the primary identifying characteristics of mammals. Humans can consume the milk of several animals, including cows, goats, buffalo, sheep, and even reindeer. Most of milk we drink, however, comes from cows.
- Technically, milk is a colloid, a dispersion of fat globules in an aqueous solution of other stuff. The white color of milk is caused by the scattering of light by these fat globules. Milk is actually a bad colloid, because given time, the fat globs rise to the top to become a layer of cream, which can be removed and processed separately. To prevent this, much milk is homogenized. In this process, the fat globules are broken up into smaller globules that don't rise and separate.
- Because milk is a natural product, it also contains natural bacteria—some of which may be harmful. So, milk is flash-heated to high temperatures to kill this bacteria. This process is called pasteurization. The U.S. Centers for Disease Control and Prevention recommends pasteurization for all milk. Milk that hasn't been pasteurized is called raw milk, and its sale is regulated in many countries.
- Milk is almost the perfect food. Its exact composition depends on the species of mammals, but generally cow's milk contains about three percent protein, four percent fat, four percent of a sugar called lactose or milk sugar, a small amount of cholesterol, and a wide range of vitamins and minerals, including calcium.
- Two important nutrients that milk doesn't have are iron and vitamin D. Newborn human babies have enough iron to last for several months, and after the first six months or so, many babies are expanding their diets, so iron deficiency is seldom a problem. If iron deficiency is a problem, however, supplements are available.

- Vitamin D is important for absorbing calcium and phosphorus, two elements needed for bone growth. Even human breast milk contains little vitamin D, so most pediatricians recommend a supplement. Children drink a lot of milk, so most milk is fortified with vitamin D.
- When treated with acid or enzymes, the fat and solids in milk coagulate together—they curdle. The small bits of solid, called curds, are the start of making cheese. And if you skim off the cream layer from unhomogenized milk and mix it for a while, the small globs of fat will coalesce into larger globs, eventually making a single, large chunk of fat that we call butter.

### **Alcoholic Beverages**

- Alcoholic breakfast drinks include Bloody Marys, tequila sunrises, and champagne cocktails. All of these drinks have ethyl alcohol in them. Commercially, all drinkable ethyl alcohol is made using anaerobic yeast fermentation, following the same chemical reaction that yeast perform when making bread.
- However, in this case, the alcohol isn't baked off; instead, it's allowed to accumulate to a certain percentage that defines the beverage: about 5 percent for beer and cider, and around 10 percent for wine. Of course, these values vary.
- At around that percentage of alcohol, the yeast cells start getting killed off, so naturally fermented alcoholic beverages can't get more concentrated than that. However, there is a way to get stronger alcoholic beverages, and that's to distill your original mixture.
- Ethanol has a lower boiling point than water, so if you heat a solution of alcohol and water, the alcohol evaporates off first. Remove this vapor and condense it, and it becomes a solution that's even more concentrated in alcohol, as much as 95 percent alcohol. This process is called distillation, and your final product is called a distilled spirit, otherwise known as liquor.

- Any naturally fermented liquid can be distilled to make liquor. Usually, the original liquid is rather complex, so when it's distilled, alcohol and water aren't the only compounds that evaporate. Other compounds are also distilled at the same time, so the final liquor has a smell, color, and taste that is characteristic of the original fermented stuff.
- Additional flavorings and colors can be added after the fact as well, or the distilled liquor can be stored in wooden barrels for a period of time, which also imparts color and flavor. In the end, depending on the original fermented material and how it was treated after distillation, we get liquors such as rum, gin, whisky, brandy, tequila, and others.
- The alcohol content of alcoholic beverages is listed as a percentage by volume, but proof is also an indication of the amount of alcohol. The current American definition of proof is that it is twice the numerical value of the percent alcohol by volume. Thus, pure alcohol is 200 proof, while many liquors that are 40 percent alcohol are 80 proof. The concept of proof is almost exclusively restricted to liquors, not wine or beer.

### Suggested Reading

Ball, *Introductory Chemistry*.

### Questions to Consider

1. Food is a very large part of most cultures. How is it important to your culture, and from what other cultures do you enjoy food and drink?
2. Soymilk isn't really milk, is it? Can you identify some similarities and some differences?
3. Are all dietary calories the same, or are the calories from fat different from the calories from protein or carbohydrates?

# Fuels and Explosives

## Lecture 16

In the same way that scientists have been searching for alternative fuels that don't harm our environment as much as they do now, they are also trying to discover newer, better, and safer explosives. Fuels and explosives have a common purpose: They provide energy that we humans adapt for a particular purpose. At the same time, however, they also have significant differences. In this lecture, you will learn about both their similarities and their differences.

### Fuels versus Explosives

- A fuel is a substance that reacts with oxygen or some oxygen-containing compound to produce useful energy. We differentiate fuels from other substances that react with oxygen and give off energy, but for no useful purpose.
- An explosive is a substance that gives off a lot of energy when it reacts. If the reaction is so slow that the energy given off isn't useful, we call it decomposition. If the reaction moves slowly through the material as energy is given off, it's called deflagration.
- If the reaction moves so fast that it exceeds the speed of sound, the reaction is called a detonation. Most of the time when people think of explosives, they think in terms of detonations, because it's that kind of reaction that causes destruction—one of the main applications of explosives.
- Another difference between fuels and explosives is that fuels typically need a second component, called an oxidizer, to react. In many cases, oxygen from the air is the oxidizer. In some specialty applications, nitrous oxide can be used.

- On the other hand, many explosives don't need a second component to react. That's because many of them already have oxygen or other atoms as part of their chemical structure that can act as the oxidizer. We say that they are self-oxidizing. This allows many explosives to detonate inside closed packages, buried in the ground, underwater, or even in the vacuum of space.
- Methane, the principal component of natural gas, has a chemical formula of  $\text{CH}_4$ , meaning that each molecule has one carbon atom and four hydrogen atoms. Oxygen molecules in the air are made up of two oxygen atoms bonded together. These two substances react to make carbon dioxide,  $\text{CO}_2$ , and water,  $\text{H}_2\text{O}$ , and give off energy in the process. The balanced chemical reaction is  $\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 + 890 \text{ kJ}$ .
- We need two oxygen molecules, and get two water molecules, in order to satisfy the law of conservation of energy, which states that matter can be neither created nor destroyed. That means that we have to have the same number of atoms of each element in both the reactants, our initial substances, and the products, the final substances.
- But what is different in going from reactants to products are the energies of the chemical bonds. The bond energies in water and carbon dioxide are much lower than those in methane and oxygen, so there is extra energy. This energy is given off to the environment, causing a few things to happen, including flame, heat, and light.
- An exothermic reaction is a reaction that gives off energy. It's this energy that's being given off that we can put to good use: We can heat things up, such as our house or a pot of water, or light up a room or the sidewalk to our front door.
- Other fuels have chemical reactions like the one for methane, but the amount of oxygen needed from the atmosphere may be different.

- Virtually all fuels give off carbon dioxide and water, the products of combustion. That's one reason you sometimes see water dripping from the tailpipe of the car in front of you—that water is actually a product of burning gasoline. But fuels also give off large amounts of carbon dioxide into the atmosphere, and we use so much fuel that the carbon dioxide gas is having an impact on global climate.

## **Petroleum**

- Other fuels burn and give off large amounts of energy, which is exactly their main purpose: to supply energy. Additional substances we use for fuel include gasoline, coal, kerosene, diesel fuel, wax, and even wood from trees. But a large part of our industrial society gets its fuel from crude oil, or petroleum.
- Petroleum is found in underground deposits and is formed from the long-term decomposition of massive quantities of dead organisms, usually plankton or algae. Over times spanning millions of years, subjected to high pressures and temperatures while buried in the ground, these leftover animal and plant bodies decompose into what is essentially a dirty mix of hydrocarbons. In other cases, impure solid carbon deposits called coal or big underground balloons of natural gas are formed.
- People dig up the reservoirs of these so-called fossil fuels to burn for energy production. In fact, the collection and processing of fossil fuels, including petroleum, is one of the major industries in our world, and it impacts finances, governmental policies, and international relations around the globe.
- The big rise in the need for petroleum came with the development of the internal combustion engine. The first reliable internal combustion engine was patented by Karl Benz, of Mercedes-Benz fame, in Germany in 1879. Since then, much of the industrialized world has come to rely on vehicles using internal combustion engines, most of which use a liquid mixture called gasoline as their fuel.

- Gasoline is a rather complicated mixture of hydrocarbon molecules containing anywhere from 4 carbon atoms to 12 carbon atoms. It also has a small amount of antioxidants to keep it from decomposing, some detergents to reduce buildup formation in engines, and antiknock compounds to prevent premature combustion of the fuel.
- In many places in the United States, a significant amount—sometimes as much as 10 percent—of ethyl alcohol is added, as well. It's added to increase the octane number (an indication of how well the engine behaves), reduce the amount of carbon monoxide given off in the exhaust, and reduce the dependence on imported petroleum.
- When gasoline burns, it makes carbon dioxide and water as the main combustion products. One gallon of gasoline, which weighs about 6.1 pounds, produces about 19.4 pounds of carbon dioxide gas and 10.1 pounds of water vapor, which eventually condenses to a liquid.
- It also produces about 10 million calories of energy, which is enough energy to bring 140 gallons of water from room temperature to boiling. Depending on the vehicle, it's enough energy to go anywhere from about 5 to about 30 miles away, which is of course its primary use—for transportation.
- Diesel fuel is another form of petroleum-based fuel that is used in some of our transportation. Diesel engines are more efficient than gasoline engines, emit less carbon monoxide, and are considered safer because the diesel fuel is less volatile. However, diesel



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**The octane number has no impact on the amount of energy or gas mileage you'd get; it's simply an indication of how well the engine behaves.**

engines are typically heavier and noisier than gasoline engines. And because diesel is a higher-temperature fraction of petroleum, it can sometimes gel or even solidify in cold weather.

## **Coal and Natural Gas**

- Two other important fuels that we use are coal and natural gas. Coal is a burnable rock that is mostly carbon, with some hydrogen, oxygen, sulfur, and nitrogen mixed in. It, too, is a fossil fuel, formed by the decomposition of plant matter exposed to large pressures and temperatures inside the Earth.
- Coal is a major fuel source for electrical plants around the world, and it's one of the largest sources of man-made carbon dioxide in the atmosphere. Almost 8 billion tons of coal are burned every year, mostly for electrical generation and heating.
- One of the problems associated with burning this much coal has to do with its impurities. Most coal is about one percent sulfur, and when sulfur burns, it makes sulfur dioxide, which is converted into acid rain in the environment. Another potential concern is mercury, which is present in coal at less than one part in 10 million. However, this still translates to almost a ton of mercury burned into the atmosphere every year.
- Natural gas is another fossil fuel that is predominantly methane,  $\text{CH}_4$ , which is a gas at room temperature. It also contains other gaseous hydrocarbons, such as ethane and propane, hydrogen sulfide, water, carbon dioxide, and sometimes helium.
- It's formed in two ways: as the ultimate piece of hydrocarbon, containing only one carbon atom, in thermal decomposition of plant or animal matter, or by various bacteria that emit methane as part of their metabolism, just as yeast emits carbon dioxide.
- Under the right geological conditions, gas can build up underground until it's discovered by digging or drilling. In many cases, natural gas is found in association with a crude oil find or a vein of coal.

- Natural gas is used as a domestic source of heat, a fuel for vehicles, and a replacement for coal in the generation of electricity. In domestic uses, natural gas is used for cooking, to run water heaters, and for central heating.
- Many communities are switching to natural gas-powered vehicles, mostly buses, because this generates less carbon dioxide for the same amount of energy generated. For this same reason, many coal-fired electrical plants are converting to natural gas.
- Gas gives off only half the amount of carbon dioxide as coal does for the same amount of electrical energy generated. Because of this, there's an environmental advantage to switch to natural gas as a fuel. But there's also the economic factor, and in the last few years, with hydraulic fracturing becoming significantly more efficient, natural gas and coal have been fighting over supremacy in the energy-generation sector.

### Explosives

- An explosive has one purpose in common with a fuel: to give off energy. But there are some big differences.
  - Many explosives are self-reacting. You don't always need to supply air or oxygen to make it react.
  - An explosive needs to give off energy quickly and suddenly.
  - An explosive typically gives off a lot of gaseous compounds to build up a huge pressure. This, in combination with a lot of energy, generates a shock wave that provides destructive force.
- Not all of these requirements are absolutely necessary. For example, mixtures of hydrogen and oxygen gas can explode, as can dust around grain elevators. Typically, though, those are accidental explosions.
- In many cases, we use explosives for a purpose—for example, to demolish an abandoned building or for mining coal or iron ore. For these applications, we want control over what we blow up.

- The earliest known explosive was black powder, also called gunpowder, invented in China in the 10<sup>th</sup> century. It's a mixture of sulfur, charcoal, and potassium nitrate, which is also called saltpeter. It's the saltpeter that acts as the oxidizer, so black powder doesn't need air to burn. It's considered a low explosive, because it burns rather slowly, but it does generate a lot of energy and gas.
- Nitroglycerin was first synthesized in 1846 and was the first explosive that was better than gunpowder. However, it's tricky to use and easy to set off. By absorbing nitroglycerin onto an inert substance, Alfred Nobel (creator of the Nobel Prizes) was able to tame nitroglycerin's nastier tendencies, and dynamite was quickly incorporated into demolition, mining, and warfare.
- Nitroglycerin detonates: It decomposes into gases that have more than 1,000 times the volume of the original material and gives off so much energy that temperatures in the immediate area exceed 9,000 degrees Fahrenheit. This generates a shock wave that can travel up to 30 times the speed of sound, and it's this shock wave that makes the true destructive force of the explosive. Nitroglycerin is an example of a high explosive, because it generates a supersonic shock wave.
- Trinitrotoluene (TNT) was first synthesized in the 1860s and was used as a yellow dye. It wasn't until a few years later that it was recognized as an explosive, because it was relatively insensitive and not as powerful as dynamite. However, TNT rapidly became common because of several advantages: It doesn't attract water, can be melted and molded easily, and can be handled rather safely. TNT needs a sharp kick from a detonator to make it explode. In many applications, TNT is mixed with other compounds that have a higher oxygen content to get more bang.
- Two current explosives are cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX). Like TNT, these compounds are rather insensitive and need some sort of detonator to explode. They're used almost exclusively by the military and can be mixed with other explosives to make a more powerful punch.

## Suggested Reading

Akhavan, *The Chemistry of Explosives*.

## Questions to Consider

1. Did Alfred Nobel's creation of the Nobel Prizes compensate for his invention of dynamite? Did he even need to compensate for inventing dynamite?
2. Ethanol is a common gasoline additive, but it causes different pollution than gasoline when it incompletely combusts. Is it proper that society should be using large amounts of ethanol as a fuel?

# The Air We Breathe

## Lecture 17

Our atmosphere keeps us alive. It has oxygen to breathe, blocks harmful ultraviolet rays, and holds onto some warmth. Our atmosphere provides us with thunderstorms, snowfalls, and rainbows. But our atmosphere is limited, and it has been demonstrated with the ozone layer that human activities can change the atmosphere—and not necessarily for the better. As you will learn in this lecture, for something that can't be seen and is rarely felt, our atmosphere has a great impact on everyday life.

### The Oxygen in Air

- To animal life, the most important component of air is oxygen. Elemental oxygen exists as a two-atom, or diatomic, molecule in its normal state. If there's a source of energy—such as ultraviolet light or a bolt of lightning—oxygen molecules can react to make a three-atom, or triatomic, molecule that we call ozone.
- Ozone is simply a form of elemental oxygen, but it's less stable than the diatomic form, so left to itself, ozone would react back to the diatomic form of oxygen. In the ozone layer, ozone is constantly being formed as the ultraviolet rays from the Sun shine on the oxygen molecules in our upper atmosphere.
- All animals need oxygen to survive. That's because in our cells, oxygen is combined with glucose, a form of sugar, to make carbon dioxide, water, and—most importantly—energy for us to live:  
$$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} + \text{energy}.$$
- The oxygen content in our atmosphere is generated by plants, either terrestrial or ocean-based. It's a symbiotic relationship, because while we exhale carbon dioxide as a product of our metabolism, plants take in carbon dioxide and, through the wonderful reactions of photosynthesis, give off oxygen.

- If there were no more plants, then animal life on this planet would eventually die off. There is no other natural process that creates as much oxygen as plants do, and even if there were, oxygen is so reactive that it would combine chemically with other compounds in the ground and the oceans.
- Only one in a million oxygen atoms is actually in the atmosphere; the rest of the atoms are tied up in rocks, minerals, and surface water. That's because oxygen is so reactive. If it weren't being constantly regenerated by plant life, it would react away, and animal life would cease to exist.
- Oxygen exists in our atmosphere at a pressure of about 3 pounds per square inch, out of a total pressure of 14.7 pounds per square inch. However, if that oxygen pressure drops by only 25 percent, to 2.2 pounds per square inch, a person wouldn't be able to survive. That corresponds to an altitude of about 15,000 feet above sea level, so many people ascending that high may need breathing support.
- At pressures of about 22 psi or higher, oxygen can actually be toxic. It can cause seizures, dizziness, confusion, and vision and hearing problems. While most of us don't have to worry about this, some do—such as divers using compressed air, doctors treating neonatal babies with pure oxygen, or astronauts in spaceflight.
- There are some forms of life for which oxygen is actually poisonous. These are called anaerobic organisms. They range from single-celled life such as bacteria, to fungi such as yeast, to baby worms that cause the disease trichinosis in pigs and humans.
- Anaerobic organisms base their cellular respiration on substances other than oxygen, such as sulfate, nitrate, or even sulfur. Less energy is given off in these respiration processes, but still enough is given off to survive. Perhaps the most common use of anaerobic organisms is the use of yeast, which makes ethyl alcohol as a by-product of anaerobic respiration and is fundamental to the alcoholic beverage industry.

## The Nitrogen in Air

- The majority of air—78 percent of it—is the element nitrogen. Like oxygen, nitrogen also exists as a two-atom, or diatomic, molecule in its elemental form. The chemical bond between the two nitrogen atoms is unusually strong, so much so that elemental nitrogen is one of the most energetically stable molecules known.
- That's why there's so much nitrogen in our atmosphere, because it's so unreactive. Unlike oxygen, it does not support life; animals kept in an all-nitrogen atmosphere quickly die, as do candle flames.
- But nitrogen is crucial for life. How does it get incorporated if it's so inert? There are several common ways. The first is lightning, which is energetic enough to force nitrogen to react with oxygen to make compounds that are eventually introduced into the life cycle.



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- **Lightning forces nitrogen and oxygen to interact, making compounds that are introduced into the life cycle.**  
Second, there are several forms of life, especially some bacteria and a family of plants called legumes, that have an enzyme that can convert the nitrogen gas in atmosphere to ammonia, a nitrogen compound that can then be used chemically to make other nitrogen compounds. This process is called nitrogen fixation. In the case of legumes—including peas, beans, peanuts, soybeans, and clover—the roots of the plant host symbiotic bacteria that react with, or “fix,” the atmospheric nitrogen.
- Of the three major classes of biological compounds—fats, proteins, and carbohydrates—only proteins have nitrogen in them. This means that anywhere in the body that proteins are important, nitrogen is important—for example, in the formation of muscle, cartilage, hair, skin, enzymes, and hormones.

- Protein in the diet is a major source of nitrogen, which is present in the form of amino acids, which are the building blocks of proteins. Most of us get protein from eating meat, which contains all of the amino acids that our bodies need to grow and thrive. Vegetarians and vegans have to get amino acids from plant sources, such as beans, peas, or nuts.

### The Discovery of Argon

- Argon is the third most common component of dry air. The discovery of argon is an interesting story. In the 19<sup>th</sup> century, the accurate determination of atomic masses was an important task for the scientist. English scientists John William Strutt, also known as Lord Rayleigh, and William Ramsay were trying to determine the atomic mass of nitrogen.
- They noted a curious and inescapable result: The experimental atomic mass of nitrogen from the air was always slightly larger than the experimental atomic mass of nitrogen isolated from a compound. They ultimately concluded that the sample from the air was contaminated by another gas and set about isolating that gas.
- From a sample of air having a volume of several gallons, they carefully removed the nitrogen, oxygen, water vapor, and carbon dioxide and were left with a small bubble of gas that, when tested with a spectroscope, proved to be a new element. They called this element argon.
- Argon was the first of a new family of elements that made a new column in the periodic table of elements. This new column, ultimately containing the gaseous elements helium, neon, argon, krypton, xenon, and radioactive radon, contains elements that are extremely chemically unreactive toward other elements and compounds.
- The reason for this is because of the arrangement of the electrons in each atom. Electrons are organized around the atomic nucleus in shells and subshells, and when an atom has eight electrons in its outermost, or valence, shell, the arrangement is especially stable

and resists change. All of the elements in this new column except helium have eight electrons in their valence shell, so they are very chemically unreactive, so much so that it inspired the name “inert gases” for this column.

- Things changed a bit in the early 1960s, when Canadian chemist Neil Bartlett discovered that the largest stable inert gas, xenon, did actually form a stable compound with other very reactive substances. To date, more than 80 stable compounds of xenon have been discovered, as have stable compounds of krypton and even radioactive radon.
- No room-temperature compounds of argon, neon, or helium have been discovered. Still, it’s clear that under the proper conditions, some of these gases aren’t “inert”—they’re just a little standoffish. So, the name “noble gases” is used today, giving an impression of privileged elements that don’t want to interact with the other riffraff elements.
- Argon has some uses in our society. For example, even though nitrogen gas is very chemically stable, there are some cases where it won’t work, so argon is used instead. Examples include welding, incandescent lights, and some automobile and bicycle tires.

### **Carbon Dioxide and Other Greenhouse Gases**

- Carbon dioxide is a minor part of our atmosphere, but it’s the cause of a major headache for society. It’s one of the main products of combustion, and the use of fossil fuels since the beginning of the industrial revolution has caused an increase in the amount of carbon dioxide in our atmosphere.
- Over the last few hundred thousand years, the  $\text{CO}_2$  concentration in our atmosphere ranged from 200 to 300 parts per million. Since the late 1950s, a carbon dioxide monitoring station on the volcano Mauna Loa has been constantly measuring the carbon dioxide content, and carbon dioxide concentrations have gone from about 300 parts per million to just under 400 parts per million.

- We know that the carbon dioxide comes from fossil fuels because of the isotopes of carbon in the carbon dioxide. Each element can have different numbers of neutrons in its nucleus, and atoms of the same element with different numbers of neutrons are called isotopes. Isotopes of the same element have exactly the same chemical properties, so when carbon isotopes burn, they'll make carbon dioxide.
- Natural carbon exists as two stable isotopes: carbon 12 and carbon 13. About 99 percent of naturally occurring carbon exists as carbon 12, while the remaining 1 percent is carbon 13. But the exact ratio of the two isotopes depends on the source of the carbon, and by studying the isotopic contents of crude oil and coal and natural gas, scientists have evidence that the carbon dioxide in the atmosphere is coming from fossil fuels.
- The reason that the increasing concentration of carbon dioxide is a concern is because  $\text{CO}_2$  is a greenhouse gas. A greenhouse gas is a gas that absorbs and emits infrared radiation, which we perceive as heat and which contributes to warming our planet; this influence on climate is called the greenhouse effect.
- Carbon dioxide isn't the only greenhouse gas in our atmosphere—water vapor, methane, and ozone also absorb and emit infrared radiation—but carbon dioxide is the only gas whose concentration has increased by one-third over the last 150 years.
- The greenhouse effect isn't inherently bad. Scientists have modeled that if it weren't for the greenhouse effect caused by water vapor, carbon dioxide, and other gases, the Earth would be about 50 degrees Fahrenheit colder than it is now, which would make living conditions on Earth significantly different.
- The amount of carbon dioxide in the atmosphere is increasing, and human activities are the main cause for this increase. At the same time, the average global temperature is increasing. One of the effects of this temperature increase is that what would

normally be ice will melt into liquid water. The only way that ice can melt is if energy is added, and this energy is coming from the warmer temperatures.

- The Arctic and Antarctic polar ice caps have both shown a decades-long trend of becoming smaller and smaller as they melt due to higher temperatures. In the case of the southern ice cap, because most of the ice lies on top of the actual continent of Antarctica, this melting ice will contribute to rising sea levels around the world.
- Increased global temperatures will affect life in the oceans around the world, including the destruction of coral reefs and the changes in the life cycles of fish, birds, and insects. And we're already seeing an impact on the weather—not just a greater occurrence of more destructive storms because a warmer temperature means more energy in the atmosphere, but also in the record-breaking high temperatures experienced around the world.

### Suggested Reading

American Chemical Society, *Chemistry in Context*, chaps. 1–3.

The Official Web Site of the Nobel Prize, <http://www.nobelprize.org/>.

### Questions to Consider

1. Explain how ozone is bad near Earth's surface but good in the upper atmosphere.
2. Too high a concentration of oxygen is not good for animal life. Is it proper to consider oxygen a poison? Why or why not?

# Materials: The Stone, Bronze, and Iron Ages

## Lecture 18

Over the course of human development, people used naturally occurring materials and slowly learned how to fabricate new materials that were even better. As human civilization developed, several types of matter were so important to the culture of the time that a historical age has been named after that material. As you will learn in this lecture, although not every culture experienced each age to the same extent as others, prehistory is often divided into three ages based on the dominant material used to make tools: the Stone Age, the Bronze Age, and the Iron Age.

### The Stone Age

- For most of prehistoric times, stone was the hardest substance commonly found. Stones, or rocks, are solid mixtures of minerals—that is, nonorganic matter—that compose the outer shell of the Earth, called the lithosphere.
- On our planet, most rocks are based on silicon and oxygen compounds called silica or silicates. Together, these two elements make up almost 75 percent of the Earth's crust by weight.
- The third most common element in the Earth's crust is aluminum, and when aluminum is combined with silicon and oxygen, it makes a type of mineral called aluminosilicates. Most clays are aluminosilicate minerals, and when dried, they can become as hard as rocks. Together, silicates and aluminosilicates compose more than 90 percent of the Earth's crust.
- The Stone Age is by far the longest age. There is evidence of stone tool use in fossilized animal remains that are more than 3 million years old. The oldest known archeological sites that contain stone tools have been dated at 2.6 million years old. These dates are

consistent with the evolution of the genus *Homo*, possibly starting with *Homo habilis*, leading to *Homo erectus*, and ultimately ending with *Homo sapiens*—us.

- Rocks are generally divided into three categories, depending on how they were formed. Igneous rocks are formed from the solidification of magma or lava from volcanic sources. Granite and basalt are two common examples.
- Sedimentary rocks are formed from the precipitation of sediment, or tiny particles in a water environment. Over long periods of time, the sediment solidifies into rock. Sandstone, limestone, gypsum, and even coal are considered sedimentary rocks.



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**Granite is a common type of igneous rock.**

- Metamorphic rocks are formed by exposure to high temperatures and pressures deep under the surface of the Earth; these extreme conditions can change the physical and chemical properties of the rock. The original rock, called protolith, can be igneous, sedimentary, or some other type of metamorphic rock. Slate and marble are two examples of metamorphic rock.
- Rocks of these different types were used differently in the Stone Age, because they have different general properties. For example, flint and chert are two types of sedimentary rocks largely made of silica. They are both very hard, but they also flake easily and, therefore, were made into sharp tools like spearheads, arrowheads, and knives.

- Basalt and sandstone were used as grinding or pounding tools, so the original hammer was actually made out of stone. Stone wasn't only used for tools. There is evidence that about 2 million years ago, prehistoric humans began using stone for shelter, either with other materials, such as branches, or, eventually, with animal skins to make rudimentary tents.
- Artificial stones, known as bricks, are commonly used as building materials. Modern bricks are mixtures of sand and clay that are fired in a kiln. The type of bricks we call cinder blocks are bricks made with cinders, the ashes left over from the combustion of coal. Cinder blocks are, in fact, the largest use of recycled ash.
- While we name the Stone Age after stone, this period of human development had other characteristics. Humanity existed largely as hunter-gatherers, essentially obtaining whatever food they could from what they found in their environment.
- Stone Age people apparently had burial rites, because both above-ground and below-ground tombs have been found all over Europe and western Asia. The earliest known examples of art and even musical instruments date from the Stone Age.

### **The Bronze Age**

- The transition out of the Stone Age is thought to have occurred in northern Africa and Europe. It came with the development of smelting, which is the process of heating of certain rocks to release their metals. The earliest known metal object is a copper axe found in modern-day Serbia that dates from about 5500 B.C.E.
- The Bronze Age was well underway by about 3000 B.C.E. It wasn't until a culture learned how to smelt the metal tin separate from copper, and then mix the molten tin with copper to make bronze, that the Bronze Age was established. Smelting, then, is one of the oldest industrial processes known.

- Smelting is believed to be more than 8,000 years old, but because it predates writing, its actual invention is obscure. Very few metals are found pure in nature; instead, they're found as compounds with oxygen, sulfur, or carbon and oxygen together. These compounds are generally known as ores.
- In order to get the pure metal, these ores need to be reacted with certain other compounds at high temperatures. The chemical reaction taking place is known as reduction. Substances that cause reduction include charcoal, which is largely the element carbon.
- At some point in history, someone realized that if you mix charcoal with a certain kind of rock and get it very hot, you can make a certain metal. Different ores ultimately yielded different metals. Occasionally, the ore had to be heated to decompose it into a simpler substance before reduction; this process is called roasting.
- Different metals needed different temperatures for reduction to occur. The earliest metals to be smelted were tin, lead, and mercury, which were being isolated from their ores by 6500 B.C.E. They were the first because relatively low temperatures were needed to smelt them—they could be produced from the heat of a campfire.
- However, they were all rather soft; indeed, mercury is a liquid at normal temperatures. Because of their softness, they weren't much utilized, except for lead, which had only a few special uses, such as slingshot ammunition.
- Lead was easy to shape, too, so later civilizations in Greece and Rome actually used lead to make water pipes. Tin was seldom used as the pure metal, especially because it was less common than lead.
- Copper, however, required higher temperatures, so smelting of copper had to wait until the invention of the oven—or, more specifically, the kiln. In fact, smelting of metals happened around the same time that pottery started to be made.

- Pure copper is also rather soft, but the oldest known pieces of smelted copper, which are about 7,000 years old, were pretty impure. Eventually, someone noticed that if two or more metals were mixed, the resulting mixture was harder than either metal alone—and, with that, alloys were invented.
- Technically, bronze is an alloy of copper, and early bronze was a mixture of copper and arsenic, because the two elements occurred together in many ores. Later bronze, by about 3000 B.C.E., was a mixture of about 90 percent copper and 10 percent tin and was harder than arsenic-containing bronze. Besides, arsenic was poisonous; it's not unlikely that makers of arsenic bronze died out.
- Bronze is harder than stone and pure copper, so it confers a distinct advantage to the bronze tool and weapon user. Therefore, bronze got used for a variety of items, including tools, weapons, decorative objects, building materials, and even armor. But the introduction of bronze to society signaled something else: the development of an advanced agricultural society.
- The domestication of plants and animals began in the late Stone Age, but with the development of bronze tools, both human and animal labor became significantly more efficient, allowing for larger, denser populations of people to survive. By this time, dogs, sheep, goats, cows, and donkeys had been domesticated, as had certain cereal crops, such as rye and wheat.
- Another Bronze Age invention is writing. Writing of numbers predated writing of language, and by 5,000 years ago, certain specific marks were used to represent certain specific numbers. Clay was a common medium for making records, some of which survived as artifacts of civilizations from long ago. Writing created permanent records so that the progress of a civilization could be detailed, and we still have some of those records today.

- The arrival of the Bronze Age also required the development of interaction among cultures. In fact, interaction became a necessity: The copper and tin ores used in smelting were seldom found in the same location, and different groups of people had to learn to trade goods or services for bronze to be made at all.
- These interactions between groups were not always pleasant; it's generally recognized that large-scale, organized warfare began in the Bronze Age, very likely because of competition for resources. Water, food, land, and other natural resources weren't evenly distributed, and if one population became too strong, that population might find it easier to take from others than to build for themselves.

### **The Iron Age**

- Iron was the last major structural metal to be smelted. Iron was known and used for thousands of years—if you were lucky enough to find a meteorite on the ground, but that was rare. Even then, for thousands of years, there was no way of getting a high enough temperature to melt the iron into different forms, so the best you could do was beat it into shape with a hammer, assuming that the hammer would survive the beating.
- Getting iron from its ore requires much higher temperatures than you can get with a pottery kiln, and it took special furnaces to reach those temperatures. These furnaces weren't invented until 4,000 years ago, in a region that is now eastern Turkey. It was only then that iron metal became available.
- Iron in its elemental state is not much harder than bronze. However, when iron is alloyed with a bit of carbon, it becomes steel and is significantly harder than bronze. And because charcoal, mostly carbon, was a common material used in smelting, a lot of the smelted iron contained a few percent of carbon and was really steel.

- Even though smelting iron was more difficult than smelting copper or tin, iron ore is much more common than copper or tin ores. Also, you can make iron from a single ore, so you don't have to rely on trade with someone else to get one of the raw materials. So, once the method for making iron metal was established, it quickly became the metal of choice for tools, weapons, and other uses.
- Alloys of iron and carbon are tricky. Iron with low carbon content is called wrought iron, which can be shaped, cut, or beaten with tools into the required shape because it is relatively soft, especially when hot. Needless to say, wrought iron isn't very strong.
- Iron with a carbon content that is too high, called cast iron, is brittle and difficult to work after it solidifies. Typically, the liquid alloy is poured into a mold and allowed to solidify. Cast iron was common in China by 500 B.C.E. and was their primary iron alloy. We still use cast iron today, in cookware, pipes, and automobile engines, but not in blades where the ability to keep a sharp edge is important.
- Just like in the Bronze Age, there were other significant sociological and cultural advances that accompanied the Iron Age. Written alphabets became widespread, and some of our oldest manuscripts, books, and other writings come from that time, whereas previously clay tablets and perhaps single sheets of papyrus are all that's left.
- Because of the toughness of iron tools, more and larger natural resources were used to construct more and larger structures, some of which survive today. Estimates of human population suggest that the number of people alive at the time grew by a factor of six from the beginning of the Iron Age to the beginning of the Common Era. City-states rose and fell. Sea travel became a major means of transport—not just of people but also of goods.
- In some respects, we're still in the Iron Age. Iron-based alloys are a major construction material, second only to concrete. In 2013, worldwide production of steel was more than 1.6 billion metric tons, mostly in China, the European Union, Japan, and the United States.

## Suggested Reading

Heizer, “The Background of Thomsen’s Three-Age System.”

## Questions to Consider

1. Which material had, or has, a bigger impact on construction in our society, stone or iron? Justify your choice.
2. Not all societies went through the Stone/Bronze/Iron Ages at the same time or in the same sequence. What are some of the natural resources and technologies needed to progress through this series?

# Again and Again: Polymers

## Lecture 19

**S**ome objects are made up of very, very long molecules. Molecules like these have certain special properties—properties that humanity started using only about 100 years ago. Some of these very, very long molecules are natural, while others are synthesized in the laboratory. While many of these molecules are complicated, their building blocks can be very simple. In this lecture, you will learn how these building blocks make some of the largest molecules in existence.

### Rubber

- Many plants give off a whitish liquid when they're injured. This liquid is called latex, and it's a complicated mixture of proteins, starches, and other stuff that quickly solidifies, forming a sort of scab to protect the remaining plant.
- In the mid-1700s, scientists noted that the solid latex from a certain South American tree could rub off pencil marks, so the material got the name “rubber.” These trees, which produced a lot of this latex, are now called rubber trees.
- The properties of rubber have to do with the molecular structure of the solid rubber. Raw latex is a solution containing molecules of a substance called isoprene, a small molecule made up of five carbon atoms and eight hydrogen atoms. The isoprene molecule has two carbon-



**The liquid produced when a plant is injured is called latex.**

carbon double bonds, one on each end of the molecule. Under the proper circumstances, the two double bonds can break one bond and, on one side, remake a double bond in the center of the isoprene and, on the other sides, link with another isoprene molecule.

- The next molecule can do this also, and so forth down the line, until a new, very long molecule of rubber is formed. The long, repetitious molecule of rubber is called a polymer, from the Greek words for “many parts.” The individual isoprene molecule is called a monomer, or “one part.”
- Rubber is bouncy because the long polymer molecules of rubber aren’t all lined up in straight lines. Also, the bonds between the carbon atoms in the polymer have angles anywhere between 109 degrees and 120 degrees. Under pressure, these bonds close up a bit, much like a pair of scissors closing.
- It doesn’t need much. Because of the thousands or even millions of bonds in any one polymer molecule, even if one bond angle closes up slightly, there’s lots of them doing it, and the cumulative effect is easily noticeable. But then the bonds move back to their normal position, generating an opposite pressure that makes the material bounce back.

### **Ethylene and Its Polymers**

- The molecule ethylene is the simplest polymer. It has two carbon atoms connected by a double bond, with each carbon atom also connected to two hydrogen atoms. Its molecular formula is  $C_2H_4$ . Under the right conditions, one of the bonds between the carbon atoms can break and point outward and make a bond with another ethylene molecule that’s doing the same thing. This can happen over and over again, until you get a molecule that has thousands and thousands of monomers, all lined up in a row.
- Polyethylene is a polymer of ethylene that has many uses in society, especially in the packaging industry. It’s used to make wrapping films, bottles and other containers, and pipes. As simple

as polyethylene is, it can get more complicated. Imagine that the molecules in polyethylene are indeed long and straight. Because of this, the molecules can pack together fairly tightly. This makes high-density polyethylene, which is used to make milk jugs as well as pipes and margarine containers.

- But ethylene molecules don't have to connect end to end all the time. In certain conditions, the bonds can rearrange, and two ethylene molecules can add to the end of the chain, and then keep growing. This is a branched polyethylene.
- The density of the polymer depends on the extent of branching, because typically the more highly branched polymers don't pack their molecules as efficiently. Depending on its density, the polyethylene has different uses, from bubble wrap to frozen food bags and from pipe fittings to toys.

### Other Polymers

- Other monomers can be used to make polymers. For example, if we take one of the hydrogen atoms in ethylene and replace it with a one-carbon branch called a methyl group, we have a monomer called propylene, and it can be polymerized to make polypropylene.
- It's used to make plastic furniture and carpeting and can even be woven into fabric for specialty clothing. It's relatively resistant to heat, so can be used for medical instruments that have to be sterilized or for eating utensils that have to go through the dishwasher.
- If we replace one of the hydrogen atoms with a chlorine atom, we have a compound called vinyl chloride, which we can use to make polyvinyl chloride (PVC). We use PVC for credit cards, to make pipes for plumbing in houses, and as insulation on electrical wires.
- If we replace one hydrogen atom with a six-membered carbon ring called a benzene ring, we get the monomer styrene, which polymerizes into polystyrene. This is used to make plastic utensils and disposable razors, but you probably know polystyrene best as

a substance that makes a plastic foam known by its trade name, Styrofoam. It has good insulating properties, so it's used to make cups for hot and cold drinks, and it's also used as a packaging material because it absorbs shocks well.

- There are other polymers, too, such as polyethylene terephthalate, which is used to make soda bottles; nylon, which is used to make hosiery; and even polymers called silicones that have silicon and oxygen backbones instead of long carbon chains.
- All of these polymers are examples that use a single monomer. There are polymers that use more than one monomer. These are called copolymers, and this is one way of varying the physical and chemical properties of the final product.
- The copolymer can be strictly alternating, with monomer number one followed by monomer number two, followed by one followed by two, and so forth. It could be periodic, with some of monomer number one followed by some of monomer number two, and so forth.
- Alternatively, it could be random, with a statistical mix of each monomer throughout the polymer chain. By using two or more different monomers, polymer makers can fine-tune the properties of the final product to their individual uses.

### **Polymer Additives**

- Polymers have some great properties, especially because there are different monomers and even different ways of mixing monomers to make copolymers. But a polymer might not have the optimal properties you want. That's where additives come in.
- The most straightforward additive is probably a color. Like any substance, polymers have their own color; pure polyethylene, for example, is clear or translucent white. For visual purposes, manufacturers may want to color a polymer, so they'll add dyes to make the material the desired color.

- Other additives are used to change the physical or chemical properties of the polymer. Many polymers are very rigid, so an additive called a plasticizer is added to make the polymer softer. Plasticizers are usually smaller molecules that are somewhat oily, allowing the long polymer molecules to slip and slide against each other more easily. Plasticizers slowly evaporate, and the physical properties of the polymer revert to their original, not necessarily desirable, state.
- Some additives are used because they're cheaper than the polymer itself and add volume with minimal cost. Additives in this category include powdered chalk, zinc oxide, and starch. Starch also helps make the polymer partially biodegradable. Plastics made from pure starch can even be added to your compost pile and will decompose completely within a year.

### **Biological Polymers: Carbohydrates**

- Most of your body tissues are polymers. In fact, DNA, which contains the instructions for life itself, is a biological polymer. Three major components of the human body are proteins, fats, and carbohydrates. Of those three, two of them are polymers: proteins and carbohydrates.
- The very word “carbohydrate” means hydrated carbon, and carbohydrates are a class of materials that can be thought of as polymers of the monomer whose chemical formula is  $\text{CH}_2\text{O}$ —carbon and water. While any molecule that has that general formula of one or more units is technically a carbohydrate, in practical terms, there are only a few real carbohydrates.
- For all practical purposes, the simplest carbohydrates are the saccharides, which is a word that comes from the Greek word for sugar. A sugar is a small molecule that makes food taste sweet, and while table sugar is a common example, there are in fact many different sugars.

- Sugars like glucose and fructose form the basis of large carbohydrates, so they are sometimes called monosaccharides. Two monosaccharides can link together as a sort of two-piece condensation polymer to make a sugar called a disaccharide. Regular table sugar is a disaccharide, called sucrose, that has one unit of glucose and one unit of fructose. Lactose, a sugar found in milk, is composed of one unit of glucose and one unit of galactose, another monosaccharide that has the molecular formula  $C_6H_{12}O_6$ .
- Oligosaccharides are polymers containing three to nine monosaccharides. All red blood cells have some four- or five-saccharide sugars attached to their surfaces. These oligosaccharides are part of your immune system.
- Polymers of large numbers—hundreds or thousands—of usually glucose monosaccharides are called polysaccharides. There are several major polysaccharides, including starch and cellulose, and they differ by the geometry of the link between the glucose unit.
- Starch is one of the main energy storage compounds for life. In our bodies, an enzyme called amylase breaks down the starch into individual glucose units, which are then transported to cells for cellular respiration. There, the glucose is broken down in the presence of oxygen to make water and carbon dioxide.
- Cellulose is a structural polysaccharide because it makes up the structural components of plants. Trees, grass, and flowers all have cellulose to keep them standing straight. Cellulose is the most common polysaccharide on our planet, and it would be a great source of food, but humans don't have the proper enzymes to digest it.

**Biological Polymers: Proteins**

- An amino acid is a small organic molecule that has an amine group, whose formula is  $\text{NH}_2$ , and an acid group, whose formula is  $\text{COOH}$ , attached to the same carbon. The simplest amino acid is called glycine, in which the other two bonds to the central carbon atom are made to hydrogen atoms. There are amino acids that contain more than 30 atoms and contain carbon- and nitrogen-containing five- and six-membered rings. There are more than 500 amino acids known.
- With amino acids, an  $\text{NH}_2$  group on one molecule could react with the  $\text{COOH}$  group on another molecule and make a condensation polymer by ejecting a water molecule, forming long chains of alternating amino acids. This long chain of amino acids is called a polypeptide or, more commonly, a protein. So, a protein is simply a polymer of amino acids.
- Proteins are copolymers; there are many amino acids that can participate in protein formation. In humans, there are 20 different amino acids that polymerize to make proteins in our bodies. In fact, those same amino acids are found in all other forms of life, with the exception of some bacteria that have up to three other amino acids.
- Of the 20 amino acids, 9 of them cannot be synthesized by the body and, therefore, must be obtained by the diet. These are called essential amino acids, and because amino acids are found in various foods, people on certain restricted diets, such as vegetarians and vegans, must watch what they eat to make sure that they get enough of the essential amino acids in their diets.
- Proteins are the second most common substance in the body, after water. They make up most of our muscle tissue, skin, and hair. They act as catalysts for biochemical reactions, and when they do, they're called enzymes.

- Some proteins, such as insulin, carry signals from one type of cell to another. And some, such as hemoglobin, carry oxygen and carbon dioxide back and forth from the cells to the lungs and back again. Protein can also be metabolized for its energy content.

### Suggested Reading

American Chemical Society, *Chemistry in Context*, chap. 9.

Ball, Hill, and Scott, *The Basics of General, Organic, and Biological Chemistry*, chaps. 16, 18–19.

Coleman and Painter, *Fundamentals of Polymer Science*.

### Questions to Consider

1. What components of the human body are actually polymers? Be as specific as you can.
2. What are the differences in reusing thermoplastics versus thermoset plastics? Is one inherently better than the other?

# Recycling Materials

## Lecture 20

**R**ecycling isn't new—for example, humanity has been composting for more than 2,000 years—but the application of recycling to materials like plastic and concrete is rather new. In addition to plastic, we can recycle metals, concrete, rubber, and other materials. Each type of material is recycled in different ways, involving different reasons and principles of science. In all instances, recycling saves on resources, energy, and cost. In this lecture, you will learn about how our society recycles materials.

### Recycling Plastics

- A plastic is any material that is moldable. There are two types of plastic: thermoplastics and thermoset plastics. Thermoplastics can be melted and reshaped without decomposing them, so they can be collected, sorted, and sent to factories to be remade into different objects. Thermoplastics do tend to degrade a bit with each reuse, so we need to be selective in how a thermoplastic is used a second or third time.
- An entire recycling industry has grown around recycling plastics, many of them community based. The single biggest obstacle to recycling thermoplastic is that it's labor intensive, even though there are machines that can help with the job. The different plastics must be separated into different types before they can be properly recycled, and the human touch is needed for that.
- In 1988, the Society of the Plastics Industry developed a symbol and number system to indicate which of the seven common thermoplastics an object is: polyethylene terephthalate, high-density polyethylene, polyvinyl chloride, low-density polyethylene, polypropylene, polystyrene, or other plastics not covered by the first six categories.

- You've probably seen the familiar triangle with arrows around it, indicating that a plastic object is recyclable. Inside the triangle is a number, and this number is specific to the particular plastic. Sometimes there are also a few letters that tell you the type of plastic the symbol refers to.



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- We recycle plastics with the goal of reducing the waste stream we create. In addition, we recycle plastics to reduce energy use. In most cases, recycling uses up to 50 percent less energy than making new plastic from scratch, and because energy costs money, recycling plastic can be less expensive than making new material. Furthermore, we recycle plastics to diminish our dependence on crude oil, which is a limited resource.
- Recycling uses up to 50 percent less energy than making new plastic from scratch.**
- Thermoset plastics like polyurethane and epoxies are molded at high temperatures and then are cured by a chemical reaction within the plastic itself; they cannot be remelted without decomposition. Recycling these plastics is more challenging.
  - Most recycling of thermoset plastics involves shredding them into tiny pieces and using the pieces as filler where needed. There's a lot of current research into the development of recyclable thermoset plastics, but currently there are none with a significant presence on the market.

## Recycling Asphalt Concrete

- The most recycled petroleum product is asphalt concrete. Although some asphalt occurs naturally, most of it comes from crude oil. It's the last part of the petroleum, the leftovers after all of the other volatile components, or fractions, have been removed.
- At room temperature, asphalt is either solid or very, very thick. It's composed of very large hydrocarbons of varying sorts, depending on the source of the petroleum. Another name for asphalt is bitumen. Pitch—a thick, tarlike substance—is also asphalt; it's used for waterproofing and making shingles for roofing.
- The largest single use of asphalt is to make asphalt concrete for road surfaces, where it's also called pavement, blacktop, tarmac, or just simply asphalt, although this last term is technically incorrect. Asphalt concrete is a mixture of about 5 percent asphalt with 95 percent gravel, sand, and crushed stones.
- Heated to several hundred degrees, the asphalt coats the stones in a thick, gooey black layer that can be spread onto the ground. As it cools down, it hardens into a solid road, driveway, or airport runway. But these roadways don't last forever. Over time, they get cracks and potholes and generally start breaking apart, so the asphalt concrete is removed and recycled, sometimes even on the spot.
- The asphalt concrete can be scraped up, heated, sometimes mixed with additional new asphalt, and relaid on the road. Asphalt concrete recycling is so good that it's estimated that only one percent of asphalt ever gets thrown away in landfills.

## Recycling Metals

- One of the most important metals in society is aluminum. Although it's the third most common element in the Earth's crust, it virtually always exists in chemical combination with other elements, especially oxygen and silicon.

- If we want to use aluminum the metal, we have to refine it from its ores. The most common ore of aluminum is called bauxite, most of which is mined in Australia, Brazil, India, and China. Aluminum can't be smelted like iron can; the chemical reactions that occur in smelting iron just don't work the same way for aluminum.
- Because of this, aluminum was historically a very rare metal, and it was very costly. In the early 1880s, aluminum was as expensive as silver and was considered precious. Today, aluminum is almost as cheap as dirt.
- In the late 1880s, American scientist Charles Martin Hall and French scientist Paul Heroult independently invented a way to extract aluminum using electricity. Electricity just started being produced in large quantities in the United States, so it was relatively inexpensive as a power source.
- Because of that, the production of aluminum was relatively cheap, and its price dropped rapidly. Combine that with aluminum's rather desirable chemical and physical properties, and aluminum began to be used to make a variety of products.
- We use electricity to make aluminum; the process is called electrolysis. We use a lot of aluminum in our society, and making aluminum from bauxite uses up about five percent of all the electricity the United States produces, and it accounts for almost half the cost of the metal product. We use aluminum for many things, including cars, doors, electrical lines, pots and pans, baseball bats, and soda and beer cans. It's even used as a powder in paints and fireworks.
- Because aluminum is an element, a pure metal, it is almost infinitely recyclable. The same sample of aluminum can be used over and over again, being reformed and reused and never losing its mechanical and chemical properties. In that regard, it's superior to plastics, which degrade slightly with each recycle. In addition, there are energy savings associated with recycling aluminum.

- Recycling aluminum is rather easy: Simply melt it, remove the small amount of stuff called dross that isn't aluminum, test the aluminum for the presence of other metals, and then add any additional amounts of metals to get the specific alloy you want. If you need very pure aluminum again, you can use electrolysis again, but in most cases, that's not necessary.
- Other metals can be recycled, especially metals that have a lot of iron in them. These are called ferrous metals, and they're used to make appliances, automobiles, steel cans, and building materials. More than 95 percent of the ferrous metals in these materials are recycled, because it costs much less in terms of materials and in terms of energy.
- Although other metals like copper, lead, silver, and gold can be recycled, there's little of it happening because they're not as common in our lives as aluminum and steel. However, there are recyclers that will accept any metal for recycling. It shouldn't take much effort to find one in your community.

### Recycling Paper

- Another commodity that is recycled is paper. Paper is lightweight, inexpensive, plentiful, and rather strong—when it's dry, that is. Get it wet, and it can fall apart like mush. In fact, that's a large part of the recycling operation.
- Paper is a thin material of compressed cellulose fibers, usually obtained from wood pulp or other plant fibers, such as cotton. Paper to be recycled comes from many places, including newspapers and magazines, home and office waste, books, cardboard, egg cartons, and even discarded mail.
- Initially, the paper to be recycled is separated into types, such as newsprint and cardboard. Then, the paper is added to a huge vat of water and is blended to break the paper up into small pieces and eventually into a thick slurry of individual cellulose fibers. This

process is called pulping. After pulping, the slurry is screened to remove non-cellulose material, such as staples and paper clips, small pieces of plastic, or globs of adhesive from sticky notes.

- But the slurry also contains tiny particles of ink that have to be removed in a step called deinking. These ink particles are removed by washing or flotation—sometimes both. Because the particles of ink are much smaller than the cellulose, by rinsing the slurry with large amounts of water, much of the ink can be washed away.
- The other method of deinking, flotation, involves adding a detergent to the slurry and then bubbling air through it. A foam of bubbles, called a froth, is formed on the top of the slurry, and the particles of ink adhere to the bubbles. The froth is skimmed off, removing the ink. This process can be repeated in stages to get the slurry cleaner and cleaner.
- Once the proper level of cleanliness is achieved, the slurry is bleached with chlorine- or oxygen-containing chemicals, washed one last time, and then laid out and compressed and dried into new sheets of paper.
- A lot of recycled paper is used to make packaging products, such as egg cartons, produce containers, and cardboard for boxes or other containers. Because of the mechanical breakdown of the original scrap paper, the cellulose fibers get broken a little each time they are recycled, so recycled paper doesn't have the strength of paper made directly from wood and plant fibers.



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**Industrialized countries recycle 50 to 75 percent of paper, saving an average of 17 trees per ton of paper recycled.**

- Around the world, industrialized countries recycle 50 to 75 percent of paper, saving an average of 17 trees per ton of paper recycled. Paper recycling also reduces water consumption, energy use, and landfill space. Many manufacturers boast of their level of environmentalism by labeling their products with the amount of post-consumer recycled paper there is in their products.

### Recycling Glass

- A major disadvantage of glass as a packaging material is that it's heavy. In part because of that, it's more expensive to transport because of increased fuel costs. Despite this, glass retains some of its consumer appeal, probably because of its transparency and historical usage.
- Glass is largely silica, which is the chemical silicon dioxide and is the main component of sand. The most common type of glass is called soda-lime glass, because in addition to silica, it has soda, the common name for the compound sodium carbonate, and lime, the common name for calcium oxide. It also has small amounts of magnesium and aluminum oxides.
- Making glass is relatively straightforward: You put all the ingredients in a furnace and melt them down. But you need a hot furnace to melt everything. After the mixture has the proper mix of ingredients and is melted down, it can be formed into plate glass, bottles, or another consumer product. Glass used for containers like bottles has a slightly different recipe than flat glass because it needs to withstand the presence of water for long periods.
- Recycling glass is very straightforward: Simply melt it down and reform it into its new, recycled product. Glass recycling is much like aluminum and steel recycling in that the recycled product is just as strong as the original, so glass can also be recycled indefinitely.
- The biggest problem with glass is that colored glass can't be uncolored, so recyclers need to separate glass by color before remelting. That makes it labor intensive.

- The second biggest problem with glass is that not all common forms of glass are recycled. Typically, only glass containers are recycled. Flat glass windows and light bulbs, even though they are also made of soda-lime glass, are typically not recycled—nor are drinking glasses and glass kitchenware.
- Remelting glass isn't the only way to reuse glass. It can be broken up into smaller pieces and used in place of gravel, saving the expense of having to buy rocks. In this form, the glass pieces can be used in concrete, asphalt, and other building materials; in mortar to help cement bricks; and in composite countertops to give a sparkly effect. It can also be ground very finely to be used as an abrasive for grinding softer materials.

### Suggested Reading

American Chemical Society, *Chemistry in Context*, chap. 9.

### Questions to Consider

1. What are some of the barriers to recycling? Can you think of ways that these barriers could be reduced?
2. One issue regarding the recycling of paper is that it's a renewable resource—it comes from trees. What are arguments for and against recycling paper?

# Resistance Is Futile: Superconductors

## Lecture 21

**E**lectricity is just electrons traveling through a material called a conductor. Most metals are good conductors of electricity. When a conductor conducts electricity, there is always a little bit of resistance to the electron flow. That resistance causes heat and robs the electricity of some of its energy. Because of this, transmission of electricity isn't as efficient as it could be. Under some circumstances, however, some materials lose all their resistance to electron flow, and electricity becomes virtually 100 percent efficient. We call these materials superconductors. We know of several and, in some cases, have adopted them in some modern technologies.

### Metals as Conductors

- Most metals are good conductors. What is it about metals that allows them to conduct electricity? The answer is in the organization of electrons in an atom. Electrons in an atom are organized into shells and subshells around the nucleus. Each shell of electrons only has a certain number of subshells, the first three of which are labeled with the letters *s*, *p*, and *d*.
- The outermost shell of electrons is called the valence shell, and because it's the outermost shell, it's farthest away from the atomic nucleus. For virtually all metals, the outermost electrons are in an *s* subshell, which is the farthest subshell away from the nucleus within any shell. That means that they are relatively free to move around.
- In our modern model of electrical conductivity, these outermost electrons are so free to move around that a sample of metal can be treated as a bunch of atoms surrounded by a sea of electrons. If we were to add electricity to one side of the metal, not only would the metal accept these new electrons easily, but it would also push out some electrons on the other side to make room. We interpret this behavior as a current of electricity.

- However, there's some resistance to the electron movement. The atomic nuclei are, after all, positively charged, and they attract the negatively charged electrons. And a metal is composed of atoms, and those atoms can get in the way of a moving electron.
- A conductor's resistance to electricity flow is called electrical resistance, and it's a physical property of the material. It's measured in units called ohms. Some conductors have a relatively high resistance; some have a relatively low resistance.
- A conductor's resistance increases with increasing temperature. This is because at higher temperatures, the atoms in the solid are moving around more and become a larger hindrance to the movement of electrons. At lower temperatures, the resistance is lower, which means that electricity flows more efficiently. It was this general trend that prompted the historical experiments of electricity at very low temperatures.

## **Superconductors**

- One of the popular areas of study in the late 1800s and early 1900s was the behavior of materials at low temperatures—hundreds of degrees below zero. For the first time in history, scientists were finally approaching the coldest possible temperature, absolute zero, as they developed new experimental techniques for achieving such cold temperatures.
- In 1908, Dutch physicist Heike Kamerlingh Onnes liquefied helium for the first time. Helium becomes a liquid at only 7 degrees Fahrenheit above absolute zero; it has the lowest boiling point of any known material.
- With his liquefied helium, Kamerlingh Onnes began investigating properties of other materials cooled down to that temperature, including the electrical properties of metals. When he cooled down a sample of mercury to the temperature of liquid helium and measured its electrical resistance, he found that it vanished.

- Kamerlingh Onnes recognized the significance of this and, in a publication announcing it, called it at first supraconductivity but later superconductivity. Over the next few years, other materials were found to be superconducting at various temperatures: lead metal at 13 degrees Fahrenheit above absolute zero, vanadium metal at 9 degrees above absolute zero, and tantalum metal at 8 degrees above absolute zero.
- Some alloys are superconductive, including alloys of magnesium and boron, niobium and aluminum, and niobium and tin. Compounds such as indium nitride superconduct, and other materials need to get even lower in temperature before they superconduct. Aluminum superconducts at 2.1 degrees Fahrenheit above absolute zero, and titanium does so at half a degree above absolute zero.
- Having zero resistance to electric current means that a current will continue to flow even if there's no additional voltage added to the circuit. Measurements of current flowing in superconducting rings suggest that the current will continue for at least 100,000 years before it stops, if not longer.
- As soon as the temperature of the conductor gets above a certain value, called the critical temperature, resistance reappears and the current starts slowing down, quickly disappearing unless additional voltage is added across the circuit.
- A superconductor also excludes all magnetic fields, a property called the Meissner effect. Normally, matter allows magnetic fields to pass through it, sometimes concentrating the magnetic field and sometimes spreading it out. A superconductor almost completely excludes a magnetic field. This leads to some interesting effects, including the apparent levitation of a small magnet over a superconductor because the magnetic field is repelled.
- There's a limit to the Meissner effect, though. If an external magnetic field is strong enough, it will penetrate the superconductor, but then superconductivity will be lost. But electrical current itself causes

a magnetic field, which means that at some critical current, the magnetic field caused by the current will make the superconductor lose its properties.

- The strengths of these critical magnetic fields and critical currents depend on the material, its critical temperature, and the size of the sample. But it seems that there are some limits to what a superconductor can do.

### **New Superconductors**

- In the 1970s, measurements showed that some metal oxides were superconductive at temperatures higher than some metallic elements—23 degrees Fahrenheit above absolute zero. This was a surprise because metal oxides are usually insulators, which don't conduct electricity, not conductors.
- Scientific experiments on additional compounds revealed substances whose critical temperature went higher and higher. Finally, in 1986, two IBM researchers named Georg Bednorz and Alex Müller found a copper oxide material that had a critical temperature of 63 degrees Fahrenheit above absolute zero, shattering the record by 20 degrees. For their work, Bednorz and Müller were awarded the 1987 Nobel Prize in Physics, only a year after their discovery.
- Since their initial discovery of so-called high-temperature superconductivity, researchers have been pushing the critical temperature record higher and higher. Currently, the record for the highest critical temperature is 134 Kelvin, which—while a cold -218 degrees Fahrenheit—is still 241 degrees Fahrenheit above absolute zero.
- There are three noteworthy things about these new high-temperature superconductors. First is their structure. They are all composed of some copper and oxygen compound called a cuprate, whose crystal structures resemble a mineral called perovskite.

- However, instead of being a pure copper and oxygen compound, the copper and oxygen mixture is intentionally contaminated, or doped, with other elements. These other elements currently include yttrium, barium, bismuth, thallium, calcium, and mercury. The exact critical temperature depends on the elements used for doping and their ratios.
- Because of the presence of oxygen, these substances aren't metals; they're not even alloys. They're actually ceramics, and part of the surprise at them being superconductors is that ceramics are usually considered insulators.
- The discovery of ceramics being superconductors has opened up the possibility that other compounds that are not normally considered good conductors may actually be superconductors at low temperatures. In fact, in the early 21<sup>st</sup> century, some iron-arsenic compounds were discovered to be superconductors, and the search continues.
- The second noteworthy thing about these high-temperature superconductors is that they are superconducting at liquid nitrogen temperatures, rather than liquid helium temperatures. Liquid helium has a temperature of 4.2 Kelvin, or about 7.6 degrees Fahrenheit above absolute zero. Any material that becomes superconductive at temperatures lower than 77 Kelvin needs to be cooled using very dangerous liquid hydrogen or the safer liquid helium.
- If the critical temperature is greater than 77 Kelvin, or 138 degrees Fahrenheit above absolute zero, you can use liquid nitrogen to cool the material. Liquid nitrogen costs about \$1.50 per gallon. On the other hand, liquid helium costs about \$60 per gallon, and those prices are fluctuating quite a bit because of uncertainties in its production.
- Nitrogen is 80 percent of our atmosphere, and the supply is virtually limitless. Using liquid nitrogen to produce superconductivity is significantly more cost effective than using helium, so it's a practical incentive to have higher-temperature superconductors.

- The final issue about these ceramic superconductors is that they're ceramics: They can't be drawn into wires, and because they're rather brittle, it's difficult to machine them into specific shapes. To date, their actual use in products has been limited. But because of their high critical temperatures and the use of liquid nitrogen instead of liquid helium, there is significant effort at finding ways to utilize these ceramic superconductors.
- Finally, the mechanism behind the superconductivity of doped cuprate ceramics is currently unknown. There are a few hypotheses about how it works—or, maybe, how it doesn't work. There's some evidence that it has something to do with the copper and oxygen combination, but for now, the actual mechanism is not understood.

### Superconductor Applications

- There are at least some special applications of superconductors. Perhaps the biggest application is for the construction of large, powerful electromagnets for use in magnetic resonance imaging systems in the medical and scientific fields.
- In this application, a sample—for example, a patient's body—is exposed to a magnetic field and to radio waves that interact with the nuclei of the atoms in the sample. By measuring the absorption of radio waves, a technician can determine what kind of atoms are in the sample, including the type of tissue in a biological sample. Physicians use this information for diagnosing diseases or injuries.



**Superconductors are used in the construction of the electromagnets in MRI machines.**

- Because of the relative size of a human body, a large magnet is needed, and the best way to get this is to use superconductor wires to make a large and strong magnetic field. It's because of this that patients have to be very careful with pieces of metal in their pockets or with metallic implants: If the implant's metal is attracted by a magnetic field, it could be very uncomfortable.
- Similar systems that use superconducting magnets are also used for a lot of scientific research, and the production of such superconducting electromagnets is a multibillion-dollar industry. For now, though, most of the applications of superconductors are still in the experimental stage or restricted to the research lab, especially when it requires large amounts of liquid helium, making a superconductor application very expensive.
- Certain very sensitive detectors are constructed from superconductors that need to be cooled to liquid helium temperatures in order to function. Superconductors are used to make particle detectors, particle accelerators, and very fast electrical circuits needed for research purposes.

### Suggested Reading

Bardeen, Cooper, and Schrieffer, "Theory of Superconductivity."

Bednorz and Mueller, "Possible High  $T_c$  Superconductivity in the Ba-La-Cu-O System."

Blundell, *Superconductivity*.

The Official Web Site of the Nobel Prize, <http://www.nobelprize.org/>.

## Questions to Consider

1. What are three barriers to widespread use of superconductors? Do you think that they will ever be overcome?
2. If liquid helium were cheap, do you think that classic superconductors would find a lot of applications? Why or why not?

# Resistance Is Useful: Semiconductors

## Lecture 22

**M**ost modern electronics are based on the semiconductor. In fact, without the semiconductor, modern electronics wouldn't exist. Instead of having desktop computers, portable phones, and electronic book readers, we'd be stuck with computers the size of whole rooms, rotary telephones that have to be wired to the wall, and televisions that take a long time to warm up. Not only do semiconductors overcome these limitations, but they also use significantly less energy than initial electronic devices. In this lecture, you will learn about semiconductors.

### Conductors versus Insulators

- An electrical conductor is a material that conducts electricity. An electrical insulator, on the other hand, does not conduct electricity. The problem with these two definitions is that there's no good dividing line between a conductor and an insulator. A physical property called conductivity can be used to express how well a conductor—or how badly an insulator—conducts electricity. But the ability to conduct electricity is a wide range, and there's no absolute way to separate conductors from insulators except by comparison.
- Materials that have intermediate conductivity are called semiconductors. What makes a material a conductor, an insulator, or a semiconductor? The model that we use is called band theory.
- The electrons in an atom have certain specific energies, called energy levels. When two atoms come together to make a molecule, their energy levels merge and even multiply, because the more electrons you have, the more energy levels you need to hold them. As more and more atoms combine, more and more energy levels come together.
- By the rules of quantum mechanics, every energy level has a specific energy value, but there comes a point when you have so many atoms, so many energy levels, that there's no real separation

between one energy level and the next. What you have, ultimately, is an energy band—effectively a continuous range of energies for the electrons.

- Electrons typically occupy the lowest energy states in the energy band. If a sample were at absolute zero, then all of the electrons would be in the lowest-possible energy states, with a maximum of two electrons per state. This is a consequence of electrons being fermions, which are subatomic particles that have a half-integer spin.
- The highest energy state that is filled in this case is called the Fermi level, and the energy of the Fermi level is important when a material acts as a conductor or an insulator. And although the value of the Fermi level is technically measured at absolute zero, it doesn't change much with temperature, so a material's Fermi level can be thought of as a property of that material.
- However, the population of the energy states changes with temperature. At absolute zero, only the lowest energy states are filled, but at higher temperatures, the energy from temperature itself can move some of the electrons to higher energy states.
- So, in addition to the lowest energy states that can accommodate electrons, there are also higher energy states that are unoccupied at absolute zero but can become occupied when the temperature increases. We say that these higher energy states are thermally occupied, or occupied with thermal energy. In fact, just like with the lower energy states, these higher energy states aren't individual energy levels but energy bands that have varying populations of electrons.
- If the energy bands near the Fermi level are only partially filled with electrons, or if there is an overlap between the Fermi level and the lowest-energy unoccupied bands, then electrons can move easily among the bands, and we have an electrical conductor. Metals are good electrical conductors.

- If there is a large gap between the Fermi level and the unoccupied band—so large that there is virtually no thermal population of the band—the material is an electrical insulator. Nonmetals like the element sulfur and covalently bonded compounds like water, whose electrons are fixed in the bonds between atoms, are good insulators.
- If the gap between the Fermi level and the unfilled band is small, then there is the chance that some electrons can bridge that gap and move among the bands. In this case, we have something called a semiconductor.
- A material that is a naturally occurring semiconductor is called an intrinsic semiconductor. Ultrapure silicon is an intrinsic semiconductor, with an electrical conductivity close to that of tap water. The issue with intrinsic semiconductors is that their conductivity is fixed; it's a property of the material.
- A material whose semiconducting properties can be modified by the addition of intentional impurities called dopants is an extrinsic semiconductor. In this case, we have more possibilities, because we can adjust the amount of dopants to adjust the conductive properties of the material. The amount of doping can vary from one part per hundred thousand to one part in 10 billion, so there's a huge range in the conductivity of semiconductors—and that's what makes them so useful.

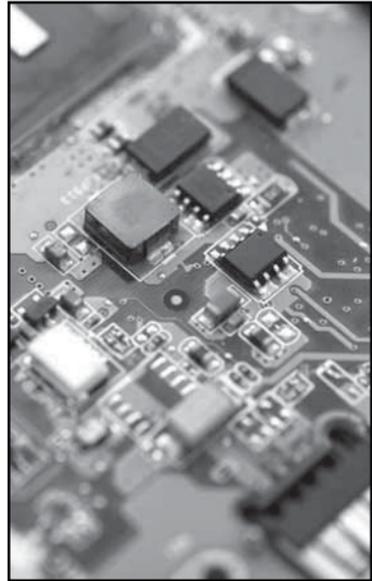
### The Electronic Structure of Silicon

- Silicon has four electrons in its highest-energy shell, called the valence shell. These valence electrons can make covalent bonds with four other silicon atoms. In pure silicon, the valence electrons are confined to these covalent bonds. But give them a small amount of energy, and a few of these electrons will break free and travel freely in a current—but only a few, which is why pure silicon is a semiconductor, not a conductor.

- Suppose that we dope silicon with a very small amount of a different element, phosphorus. A phosphorus atom has five valence electrons, so when it makes four covalent bonds to surrounding silicon atoms, it has one electron left over. It's a lot easier for that lone electron to move around in energy bands because it isn't part of a covalent bond.
- Because of this, the conductivity of the material rises. Because the electron has a negative charge, we call this an *n*-type semiconductor. The actual conductivity of the semiconductor depends on the amount of dopant used, so we can control the conductivity by controlling the amount of phosphorus we use as an intentional impurity.
- Another way we can affect the conductivity of silicon is by adding a dopant like aluminum. Aluminum has only three valence electrons, so when it gets inserted into the silicon lattice, it's missing an electron, and there's an opening where that electron would normally be. This opening is called a hole, and a hole affects the conductivity of the silicon just like an extra electron does.
- Because the lack of a negatively charged electron is a net positive charge, we call this a *p*-type semiconductor. Again, we can adjust the actual conductivity of the silicon by varying the exact amount of dopant aluminum.
- In cases of both *n*-type and *p*-type semiconductors, while we're changing the electrical conductivity of the silicon, the piece of doped silicon does not have an overall electrical charge.
- Semiconductors can be used as conductors or resistors if you need a weak example of either one. That's the whole point of a semiconductor: They are rather poor conductors of electricity, left by themselves.

## The Transfer Resistor

- When you layer a  $p$ -type semiconductor and an  $n$ -type semiconductor together and then try to send a small electrical current through the  $p$ -type layer, not much current flows—the  $p$ -type layer is, after all, only a semiconductor.
- But if you attach an electrode to the  $n$ -type layer and charge it up with even a small voltage, some of the charge from the  $n$ -type layer, which has excess electrons, will spill into the  $p$ -type layer. This spillage will dramatically increase the current flow through the  $p$ -type semiconductor. We've just made a very sensitive switch.
- We can significantly increase the conductivity of the  $p$ -type layer by adding a small extra charge to the  $n$ -type layer, essentially turning the  $p$ -type conductivity on and off by placing a small charge on the  $n$ -type layer.
- This type of construction, and the verification that it would act like a switch, was first made by physicists John Bardeen, William Shockley, and Walter Brattain in 1947 and 1948 at Bell Laboratories. It was called a transfer resistor, shortened to transistor, by the team, who went on to win the 1956 Nobel Prize in Physics for their work on semiconductors.



**Transistors changed the entire landscape for electronic devices, and are the basis of modern computing.**

- The transistor, with its layers of semiconductors, had a huge impact on the development of electronics all over the world. Transistors eventually replaced vacuum tubes in applications. Transistors are

not only a preferable technology, but their invention changed the entire landscape for electronic devices. In fact, transistors are the basis of modern computing.

- All of the advantages of transistors—including low power, low waste heat, and ruggedness—also apply to modern computers. There’s one other advantage: The smaller the transistor, the faster they react, so the faster the computer works. All of these advantages have had significant impacts on our daily lives.
- The first transistor, invented in 1947, was a few inches on a side. However, as transistors found more uses in electronics, they became smaller and smaller. While some are still a decent size, others have become so small that they’re not even visible to the naked eye.
- Transistors at the tiniest scale aren’t made mechanically—they’re made photographically. Transistors this small aren’t made individually and then wired together. Instead, entire circuits made of transistors, wires, and other components are made simultaneously; such a construction is called an integrated circuit.
- In 1965, the cofounder of Intel, Gordon Moore, put forth the idea that transistors will continue to become smaller and even stated that the number of transistors in an integrated circuit would double every two years. This statement was remarkably prescient and is sometimes called Moore’s law.
- As our technology has become better and better, we’ve been able to put more and more transistors into an integrated circuit, with a corresponding increase in speed and efficiency. But it won’t—and can’t—go on forever. Some electronics experts suggest that we’re already near the limit and that increases in transistor density and speed are already slowing. Other experts think that we still have two or three decades of improvement left, while even others suggest that transistor density will continue to increase as new ways to engineer integrated circuits are developed.

## Other Semiconductors and Their Uses

- Silicon is by far the most common basis for a semiconductor, but it's not the only one. In fact, one of the first semiconductors studied was copper oxide, which is ironic given that some modern high-temperature superconductors are based on copper oxides. Another common basis for semiconductors in modern use is germanium, which is the element beneath silicon in the periodic table.
- Speaking of the periodic table, one other tactic to getting a semiconductor is to make a compound of one element that has one less electron than silicon plus one element that has one more electron than silicon. In fact, compounds like gallium arsenide and gallium nitride are used for semiconductors and represent the primary industrial use of the element gallium.
- And if silicon and germanium are natural semiconductors, what about mixtures, or alloys, of those elements? In fact, a mixture of the elements silicon and carbon called silicon carbide is used as a semiconductor.
- In addition to their use in transistors, semiconductors are used for purposes other than integrated circuits. Perhaps the most important non-transistor use of semiconductors is the light-emitting diode (LED). LEDs have the same advantages as light sources as transistors have over vacuum tubes: They are much smaller, use much less energy, generate much less waste heat, are much cheaper, and are much more rugged.
- As production increased since the late 1960s and through the 1970s, LEDs found more and more applications, until today LEDs are being marketed as replacements for incandescent and fluorescent light bulbs. While their up-front costs are still rather high, because of their long lives and low energy usage, they are less costly to operate over the lifetime of the light, which for LEDs can be decades.

- If you engineer your light source properly, you get light amplification by stimulated emission of radiation—a laser. LEDs can be fashioned into lasers, which are called diode lasers. Diode lasers are the most common form of laser. In 2004, more than 700 million laser diodes were incorporated into a variety of electronic devices, including computer mice, laser pointers, copy and fax machines, and scanners.

### Suggested Reading

Bube, *Electrons in Solids*, chaps. 7, 9.

The Official Web Site of the Nobel Prize, <http://www.nobelprize.org/>.

Popular Science, [www.popsci.com](http://www.popsci.com).

Scientific American, [www.scientificamerican.com](http://www.scientificamerican.com).

Vardalas, “Twists and Turns in the Development of the Transistor.”

### Questions to Consider

1. *P*-type semiconductors have fewer electrons than normal, while *n*-type semiconductors have more electrons than normal. Can there ever be a semiconductor that has just the right number of electrons? Why or why not?
2. Why can't a transistor be made from two different metals, rather than two types of semiconductors?

# Out of Many, One: Composites

## Lecture 23

**A**s you will learn in this lecture, composite materials allow us to be more selective about the properties we need in a product. We're no longer completely bound by the inherent properties a substance has; we now have the ability to customize those properties to some extent, making parts that are stronger, lighter, more flexible, and more durable. Usually, they're also more expensive, because making a composite material takes more effort or requires more high-tech, costly ingredients or processes. However, in the long run, these additional expenses are worth it to have engines that operate more efficiently or football helmets that are more protective.

### Composite Materials

- A composite material is a material made out of two or more individual materials that have different chemical or physical properties. When combined, the composite material has properties that are different, usually better, than its components. Composite materials can be stronger or lighter than the single substance or may have chemical or physical properties that are better in the combination than in the single substance.
- Composite materials are composed of two main components: the matrix and the reinforcement. The matrix can be thought of as the solvent, if a composite itself were thought of as a solution. It's the material that could conceivably make a piece or a part all by itself.
- Typically, the matrix is some kind of plastic, polymer, or resin that can be molded to the desired shape. The reinforcement is the component that's mixed in with the matrix. Its job is to add toughness and stiffness to the matrix, increasing its physical performance. But how does the reinforcement do this?

- At the microscopic level, when the matrix is subjected to forces higher than it can withstand, it breaks. It starts breaking with the formation of tiny cracks that propagate through the material, until eventually the crack goes completely through the piece, resulting in two pieces. But when the reinforcement is present, it halts the growth of the tiny cracks.
- For example, the reinforcement can be long, thin fibers of some other material, such as glass or carbon. Even though the thin fiber might itself be brittle, if the initial tiny crack meets the fiber on its side, along its long axis, it can't break the fiber and the crack stops propagating. Ultimately, then, this creates a stronger material.
- Another example of reinforcement is powdered rubber added to the matrix. When a crack begins in the matrix and hits a rubber particle, the rubber stretches a little bit rather than letting the crack continue. In this way, a material that isn't necessarily hugely strong itself, rubber, can strengthen a material by keeping these tiny cracks from becoming bigger cracks, and a stronger composite material is made.
- One example of a natural composite material is wood. The cells that make up wood are long and thin, resembling tiny straws. Wood also has tiny vessels embedded in it that serve to transport water and nutrients throughout the living tree. This combination of long, thin cells and hollow vessels makes for a natural composite material.
- In addition, every year, a new layer of cells grows on the outside of the tree, just under the bark. It's this annual growth of new cells that leads to the production of the so-called rings in a tree. Between the long and thin cells, the vessels, and the concentric rings of new growth, wood is relatively light but strong and is still used today as a major construction material because of its mechanical properties.

- A classic example of an artificial composite material is concrete, which was used in ancient Greece as far back as the 14<sup>th</sup> century B.C.E. It starts with cement, a substance made from pulverized rock and ash that's been added to lime, or calcium oxide, and mixed with water into a slurry. Chemical reactions with water or carbon dioxide from the air transformed the slurry into a solid form.
- When cement is mixed with sand or small stones referred to as aggregate, it makes concrete, which has more strength than cement alone. Concrete can be pulled apart relatively easily—for a material resembling rock, that is—so in some construction, it's common to embed steel bars inside, making reinforced concrete. Concrete is the most common construction material in the world, with society using twice as much as it uses steel, wood, aluminum, and plastic combined.

### Carbon Fibers

- Carbon is an interesting element: In one crystal form, it makes graphite, a material so soft you can write with it, while in another crystal form, diamond, it makes one of the hardest substances known.
- But crystal forms aren't the only way we can get carbon. If you take a polymer thread composed of polyacrylonitrile, rayon, or even pitch from crude oil and subject it to intense heat—such as 4,000 degrees Fahrenheit—you can drive off all of the other atoms and leave the carbon atoms behind. You've just made carbon fibers.
- Carbon fibers have a range of physical properties depending on their source material and how they're made, but in general, they're only about 5 to 10 micrometers wide—about 200 to 400 millionths of an inch.
- The structure of carbon fiber is complex, although its exact structure depends on the starting material and the method of processing. Much of the carbon is in graphite-like form but is not very crystalline. Rather, the sheets of carbon atoms are arranged somewhat haphazardly instead of orderly, an arrangement called turbostratic.

- The sheets are oriented along the long axis of the fiber, and it's within the sheet that the carbon-carbon bonding is the strongest. So, the fiber's strength comes from the fact that these thin sheets of randomly arranged graphite exist along the length of the fiber.
- Despite their size, carbon fibers have some interesting properties. For example, they have two to eight times the strength of steel, meaning that it takes two to eight times more force to break two pieces having the same cross section.
- Carbon fibers require twice the force to stretch, meaning that they are less elastic and stiffer. They're also significantly lighter than most metals, so you get a better performance with less weight. However, they are very narrow and rather short, only about one to three hundredths of an inch long.



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**The strong and lightweight characteristics of carbon fiber composites are beneficial in the production of many kinds of machine parts, including propeller blades.**

- An individual fiber may have superior physical properties, but it's difficult to use a single fiber because it's so small. Carbon fibers can be woven into threads, however, and even these threads have better properties than many structural metals. The threads can be woven into fabric, and the fabric is used in composite materials.
- Carbon fiber–reinforced composites are used in aircraft and boat or submarine parts, wind turbine blades, automobile bodies, bicycles, and sporting goods (such as tennis rackets, football helmets, and golf clubs)—all of which benefit from increased strength and decreased weight.
- Worldwide, carbon fiber production is a 20-billion-dollar industry that is growing between 5 and 10 percent per year as new applications are found. One new area for carbon fibers is using them to strengthen metals and metal alloys, especially aluminum, in attempts to make them lighter, stronger, and less subject to mechanical fatigue.

### Other Fiber Composites

- Carbon fibers aren't the only fibers used to make composite materials, although they may be among the most high tech. The most common fiber used in composite materials is glass. Glass fibers were first made in the early 1930s, and the commercial applications of this so-called fiberglass were quickly realized. By 1936, plastic resins were developed to encase the fiberglass to make moldable parts, and the applications soon followed.
- Glass fibers have advantages similar to carbon fibers. They are very strong in the direction of the fiber but easy to crack across the long axis. Because of this, when making composite materials, the maker needs to make sure that the fibers are oriented in the direction where added strength is necessary.

- If strength is necessary in more than one direction, woven fiberglass fabric can be used. Fiberglass composite materials are typically two-dimensional flat or curved pieces, such as automobile bodies, hot tubs, surfboards, or diving boards.
- Glass fibers are relatively easy to make: Molten glass is passed through a nozzle that has hundreds of holes in it for the glass to come out in thin fibers. The fibers are either coated with a thin layer of coating to protect them and wound on a bobbin, or coated with a binder and sprayed onto a surface to make a mat of fiberglass. Because of the dangers of asbestos, glass fibers have replaced asbestos in many applications, although tiny pieces of glass fibers can also cause lung irritation if breathed in.
- Polymer fibers can also be used as reinforcements. One interesting polymer is composed of two monomers: 1,4-phenylenediamine and terephthaloyl chloride. The ends of these two molecules react to bond together in an alternating fashion, making a long chain or polymer.
- One of the interesting properties of these polymer chains is that they can interact fairly strongly with adjacent chains, making a solid polymer that's very strong. If you dissolve this polymer in the right solvent and then spin it into fibers, you can use these fibers, which are very strong, as the reinforcement in a composite material.
- This results in a material called Kevlar, so strong that it's used to make bulletproof body armor for police and the military. It's even used to reinforce the walls of combat vehicles, including tanks and even naval vessels, and can be woven to make material and rope.

## Nanocomposites

- At the extreme end of composite materials are nanocomposites, which are composites where one of the components has a physical dimension of less than 100 nanometers, about a millionth of an inch. So, some of the fiber-reinforced composites might be considered nanocomposites. Certain natural materials can be classified as nanocomposites, such as some mollusk shells, but most nanocomposites are synthetic materials that have specialty applications.
- One type of nanocomposite is a ceramic matrix nanocomposite, which has a ceramic as its primary component. Ceramics have some very useful properties: They are hard, can be formed into different shapes, and stand up to wear rather easily. However, they are brittle, not very flexible, and don't conduct electricity or heat very well.
- If you incorporated a small-enough percentage of fine metal powder or fibers into a ceramic, you can still have the strength of the ceramic but also have the advantage of flexibility or electrical and thermal conductivity. Ceramic composites are finding use in engines and turbines, where extreme conditions of temperature and stress require the use of materials that can best withstand those conditions.
- Another type of nanocomposite is the metal matrix nanocomposite, which switches the roles of matrix and reinforcement: A metal or alloy is the matrix, and embedded in it is some sort of nonmetal or ceramic nanomaterial.
- One of the most studied reinforcements is the carbon nanotube. Instead of being a thin fiber, a carbon nanotube is a cylinder where the wall is made from carbon atoms, almost a type of carbon molecule. These carbon nanotubes can be formed from vaporized carbon under certain experimental conditions, and they have physical properties that surpass even carbon fibers. However, currently they aren't very economical, and the use of carbon nanotubes as reinforcements in metals is still being developed.

- Perhaps one of the most unusual nanocomposites is the aerogel, which is a solid matrix that has tiny bubbles dispersed in it—it's actually more than 98 percent bubbles. They're not a gel; they're actually a solid. But the tiny bubbles in them drastically change the properties of the solid. For example, aerogels are excellent thermal insulators, and despite their extraordinary lightness, they are unusually strong.
- Aerogel production is a 500-million-dollar industry in the United States alone, and these unusual nanocomposites are finding use as insulators. They can also be used as catalyst supports and as water and gas purifiers. We're only beginning to explore the possibilities of these unusual materials.

### Suggested Reading

Jones and Ashby, *Engineering Materials II* (see references on composite materials).

### Questions to Consider

1. How many different ways is a carbon material showing up as a reinforcement? Do you think that other elements can be applied in these ways, or is carbon unique?
2. Are all composites used as construction materials? Can you name some examples of composites that are not?

# The Future of Materials

## Lecture 24

In most modern societies, progress is continuous, and part of that progress includes the development of new materials. We can use these new materials to make new products, or these new materials will have desirable properties that we can adapt into new inventions. We're limited by the matter that we find around us, and we must use the raw materials that nature provides for us. As you will learn, we still have many combinations of these raw materials to explore, and we never know what combination might make a new material with new properties.

### **New Materials from the Space Program**

- The so-called space race to land on the Moon was as much political as it was scientific. Starting in June 1969 and for the next three and a half years, six missions delivered 12 human beings to the surface of the Moon and returned them safely to the Earth. To date, no other humans have visited the Moon.
- Many people have argued against the Moon landings, claiming that just as much could have been learned using robot landers, with much less expense and significantly less worry over the potential loss of life. However, the space program wasn't, and still isn't, simply about the primary mission. Subsidiary technological advances have accompanied our drive out into space.
- Because vomiting in a space suit isn't particularly fun, NASA went to great lengths to make sure that the astronauts didn't suffer from food poisoning on their trips. They developed a seven-step system to ensure food safety, and two decades later, the U.S. Food and Drug Administration adopted NASA's system for nationwide application. In one year, the number of salmonella food poisoning cases dropped by half. Even with that, there are still about 500 deaths per year due to salmonella poisoning in the United States.

- For best launching capability, NASA has one of its major launch facilities in Florida, at the Kennedy Space Center. Unfortunately, it's rather hot and humid there. To protect the launchpads from the hot, humid, corrosive Florida weather, NASA invented a protective coating for their buildings and equipment. At least two other prominent structures in similar environments, the Statue of Liberty and the Golden Gate Bridge, are now also coated in the same material.
- Teflon-coated fiberglass was an original component of space suits and now has multiple non-space-related uses—most famously, the fabric top of the Metrodome in Minneapolis.
- A lot of the energy provided in spacecraft comes from batteries—but special types of batteries called fuel cells. Much of the thrust in large rockets comes from the reaction of liquid hydrogen with liquid oxygen. These two elements burn to make water, giving off so much energy that a Saturn V rocket can achieve Earth orbit.



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**The fabric top of the Metrodome is made with Teflon-coated fiberglass.**

- In more controlled conditions, hydrogen and oxygen can react together to produce electricity, just like a battery. These types of batteries are called fuel cells. Fuel cells were the electricity sources of choice for manned spacecraft, in part because they also produced water. They also produce no pollution, making them environmentally neutral. They are expensive, but because of their advantages, they are experiencing a resurgence in interest as a modern research topic.

## Materials of the Future

- In our electrified society, we have to transfer electricity from an electrical generation plant to the end user through wires. In the United States alone, there are about 7,000 power stations providing 4,500 terawatt-hours of electricity per year. That's enough electricity to light a single 100-watt light bulb for just more than 5 billion years.
- But about 30 percent of that energy is lost due to the resistance of the wires used to transmit—lost to heat. Imagine how things would change if instead of losing that much energy we could put it to productive use, or decrease the price of energy accordingly. This illustrates how much better off the world would be if we had room-temperature superconductors.
- Superconductors were discovered in the early 1900s. At first, superconductivity required cooling substances like mercury down to liquid helium temperatures, just a few degrees above absolute zero. In the 1980s, a new class of superconductors was discovered that would superconduct when cooled with liquid nitrogen, which is much more common and much less expensive than liquid helium. But it still requires liquid nitrogen. A room-temperature superconductor would conduct without resistance and without having to be cooled.
- The recent rise of inexpensive 3D printers is transforming whole industries. One of the technologies used by these printers is called fused deposition modeling (FDM), in which three-dimensional parts are built up by melting plastics in thin layers. By depositing plastic in just the right place as a print head rasters back and forth, a three-dimensional object can be built up. A variety of plastics can be used, as long as they melt under heat.
- The problem is that these plastics don't conduct electricity, so while 3D printers might be useful at making some objects, they're not good at making any kind of complete electrical circuit—yet. We need a substance that acts as an electric ink that can be used in 3D

printers to print electronic devices just as easily as we can print a yo-yo. Because of the significant expansion of 3D printing in the past few years, with prices and availability dropping substantially, perhaps the desire to print electrical devices will spur development of electric ink.

- Electrically conductive ink wouldn't just be useful in 3D printers; any kind of writing or printing can be made to conduct electricity. We already have ink that can be read magnetically; in fact, many checks have a series of numbers on the bottom that are written in an ink that contains iron oxide, which can be detected magnetically. But we don't have a good ink that we can use to make electrical circuits that can conduct enough of a current for modern applications.
- In the future, we need a better understanding of a whole class of materials: nanoscale technologies. Nanoscale is when objects are 1 to 100 nanometers in size, or about 30 to 3,000 billionths of an inch wide. This is only about 2 to 200 atoms across. At this scale, we're entering the world of atoms. The laws of quantum mechanics become more important at this scale, so how will those objects behave when they interact?
- It's virtually certain that they will behave completely differently from how they do at the macroscale or even microscale. At the nanoscale, a single chemical bond can have a significant impact on the energetics of the system; at larger scales, individual chemical bonds can be ignored, but not at the nanoscale. What will we discover when we start looking at matter in its nanoscale forms?



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**The rise in inexpensive 3D printing is transforming industries around the globe.**

- We've already seen some hints of what we'll find, with the discovery of the quantum dot. A quantum dot is a tiny crystal that is so small that the rules of quantum mechanics, rather than Newtonian physics, control how it behaves.
- The most obvious and striking behavior of quantum dots is how they glow when they're excited by ultraviolet light or electricity. The color they glow depends on their size, too, so we can actually tune the quantum dot to give off just the right color of light. In 2013, the first flat-screen televisions using quantum dots were sold, so we're already using this nanotechnology to make products.
- One possible use of quantum dots is quantum computing, which uses the rules of quantum mechanics instead of microprocessors as the basis of a computer. We aren't at the point of development yet, but it's an illustration of the new frontiers that are possible when we get to the nanoscale.
- Another future goal is for people to live in good health for as long as possible. We rely quite a bit on the field of medicine for that—and on medicines, as well. What we want is a drug that targets a particular disease but has no negative side effects. The phrase that exemplifies this desire is “magic bullet.” Probably no disease needs a magic bullet treatment more than cancer.
- In cancer, a group of diseases that involves uncontrolled cell growth, the goal is to kill the cancer cells without killing healthy cells. Needless to say, this is a difficult task. A proper cancer drug would target the cancer cells and only the cancer cells, leaving healthy cells alone to continue their proper metabolic function.
- Matter behaves differently in a magnetic field—differently in ways that can be useful. For example, when a person gets an MRI, the first thing that happens is that they're placed inside a very large magnet. Atoms in a magnetic field can absorb radio waves that they can't otherwise, and we can use this behavior for medical purposes.

- It would be great if we could produce much, much stronger magnets than we have now. The strongest permanent magnets we have are made from elements that are relatively rare, whose supply is controlled by only a few countries. Stronger magnetic fields can be produced by electromagnets, but then you need electricity. What would be most convenient would be to have much, much stronger permanent magnets.
- Magnetism in matter is caused by unpaired electrons, which is one reason why many permanent magnets are composed of metals like iron, cobalt, and nickel. But modern materials have only begun to consider other molecules that might have unpaired electrons.
- In fact, organic molecules, molecules based on carbon, might be able to support unpaired electrons and generate magnetic fields. We wouldn't have to rely on foreign countries for raw materials if we could easily produce magnets. There's a lot about magnetism that has yet to be explored.
- Finally, we need to recognize that nature produces materials whose properties far outshine the properties of man-made compounds. Consider, for example, the spider web. Spider silk has the strength of high-performance steel but only one-sixth the density. Pound for pound, that makes it six times stronger than steel. It can also be stretched up to five times its original length before breaking. Think of what we could build if we could produce synthetic spider silk commercially.
- There are many materials that are produced naturally by plants and animals whose properties far outshine the properties of man-made objects. The intentional imitation of naturally occurring behavior or materials for human application is called biomimicry. By studying the properties of naturally occurring materials, especially materials produced by other living things, scientists and engineers hope to create new materials that can make our lives even better.

- We can get better ceramics by studying seashells. We can use the model of hollow polar bear fur to develop better insulators for our homes, cars, and clothes. The hydrodynamic propulsion system used by octopuses and squid can inspire new ways to move boats and submarines, and perhaps the airplanes and helicopters of the future will resemble the bumblebee instead of the eagle.
- It's very likely that plants have natural pesticides and other biochemical weapons that will be future wonder drugs, just as the ancestor of aspirin was found in willow bark. Nature provides one of the greatest laboratories for new materials; all we need is to properly study it.

### Questions to Consider

1. What's on your personal wish list of new materials that society should develop?
2. Can you explain how difficult it is to predict the development of new materials and the new technologies based on them?

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### **Internet Resources**

The Official Web Site of the Nobel Prize. <http://www.nobelprize.org/>. Has quite a bit of historical information on discoveries that were eventually recognized with Nobel Prizes in the sciences.

Popular Science. [www.popsci.com](http://www.popsci.com). Often has articles or discussion on the future of science.

Scientific American. [www.scientificamerican.com](http://www.scientificamerican.com). Often has articles or discussion on the future of science.