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Chemistry and Our Universe

How It All Works

Course Guidebook

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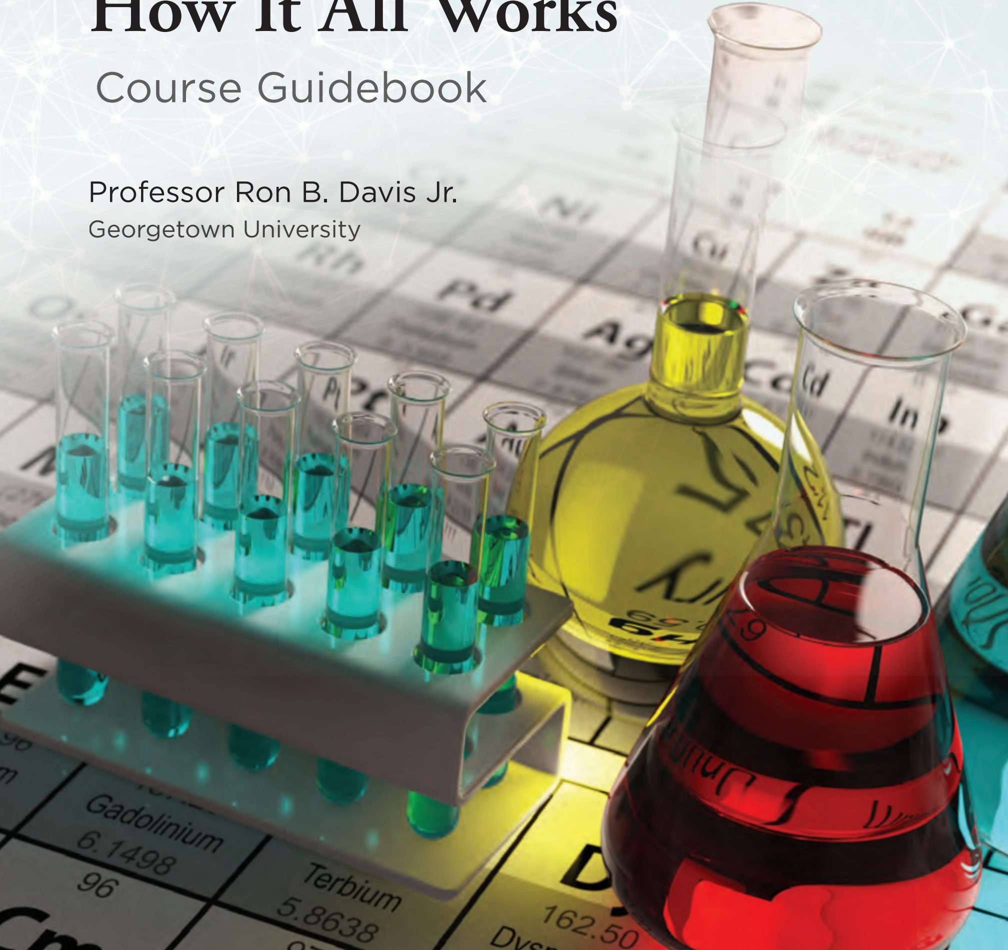

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DISCLAIMER

This series of lectures is intended to increase your understanding of the principles of chemistry. These lectures include demonstrations in the field of chemistry, performed by an experienced professional. These demonstrations may include dangerous materials and are conducted for informational purposes only, to enhance understanding of the material.

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Chemistry and Our Universe: How It All Works

COURSE SCOPE

Since the beginning of recorded history, humankind has sought to understand the properties of materials. Why does iron rust over time while gold remains shiny and beautiful? What causes the deep green color of tree leaves to convert into a brilliant variety of colors as fall approaches? How do clouds form and dispense rain? These and many other questions perplexed the minds of great thinkers millennia ago.

In the 1600s, now-iconic investigators such as John Dalton and Isaac Newton started to apply a new technique to understanding matter that involved not just observing and theorizing, but manipulating systems and observing the effect of their changes in what is now called the scientific method.

These and other great scientific explorers elevated chemistry from its alchemical roots to a bona fide science. Contributions include those of such great minds as John Dalton, who offered the first experimental evidence of fundamental particles; Antoine Lavoisier, who is credited with the first correct identification of a chemical element; and Dmitry Mendeleev, whose now-famous table of the elements helped demonstrate the ordered and predictable properties of elements in nature.

Chemists study all things made of matter as well as the energy that flows through them as they interconvert and interact. No substance or process is outside of its realm. What distinguishes chemists from all other scientists is not what they study, but the scale at which they study it.

Chemists focus on the properties and behaviors of fundamental particles called atoms—particles so small that billions of them could rest on the head of a pin. Remarkably, by understanding the structure and interactions of atoms, the materials that they comprise can be explained and even predicted with great accuracy. Materials that we see every day (such as our Sun), hold in our hands (such as tools made of metals), and even our bodies themselves all can be understood and explained scientifically. The first step on that journey is to understand the most fundamental particles making up all matter and the forces that govern their behavior.

In this course, you will be introduced to the fundamental mathematical laws governing the behavior of matter. You will explore the properties and makeup of light, atoms, and molecules, all of which play critical roles in how matter in our universe behaves and interacts. Attention will be given to the phases of matter, the most common of which are solids, liquids, and gases. Even phases such as supercritical fluids that are less common but no less important to modern technologies and natural chemical processes will be approached.

Next, you will move on to laws governing such diverse concepts as the interaction of light and matter, chemical reaction rates, the phenomenon of chemical equilibrium, the chemistry of acids and bases, and the storage and release of electrochemical potential in so-called redox reactions.

Once you have mastered the fundamentals of chemistry, you will put your knowledge to work to explore an even wider variety of topics. Time will be spent exploring how chemistry has contributed to some of humankind's most influential inventions, including the quests to find and develop useful medicines, devise powerful weapons, and even harness the stunning power of the atom itself to help satisfy humanity's power needs.

Not to be outdone by humankind, nature offers a wide array of chemical reactions and materials to study, understand, and even use to our benefit. You will use laws and ideas developed by centuries of research to analyze the chemistry we see in nature every day. From explaining the magnetic field of the Earth to solving the problem of ozone depletion in the upper atmosphere, the chemistry of our home in the cosmos will offer much to study. Finally, you will consider the cosmos and ask how chemistry can contribute to our understanding of life's origins in our universe.

Along the way, many of the founding fathers of the discipline of chemistry will be discussed. Much more than just names attached to equations or concepts, these men and women were complex people who were influenced by one another and the times that they lived in.

This course endeavors to cover a great deal of topics. As varied as those topics are, in each case, you will discover how understanding the structure and behavior of matter at the atomic and molecular levels influences the properties of matter that we all observe on the human scale every day.

Is Chemistry the Science of Everything?

LECTURE 1

Chemistry can be defined as the study of matter. But because everything in the universe is made up of matter and matter can be converted into energy, this oversimplified definition would basically mean that chemistry is the study of everything. In this lecture, you will learn about the fundamental elements of matter by learning about the periodic table of the elements—one of the most recognizable and powerful scientific tools ever devised.

CHEMISTRY: THE STUDY OF EVERYTHING

› Chemistry is the study of everything—but it does have a focus. It is defined not by what subject is studied, but rather by the scale at which that subject is studied. Chemists occupy themselves studying the universe at the atomic or molecular level.

› While a particle physicist may be concerned with the interactions and behavior of the fundamental particles of the universe—or a biologist might be interested in studying the behavior of organelles in living cells, speciation, or entire ecosystems—a chemist is concerned with the scale which falls firmly between these 2 disciplines: the scale of atoms and molecules.

› In chemistry, we study not only atoms, which are about one-tenth of a nanometer across, but also conjoined groups of atoms called molecules, which can form in a range of sizes from a fraction of a nanometer to molecules of tremendous size, such as DNA, which can stretch to lengths billions of times larger than individual atoms, creating structures centimeters in length.

- Objects just a few centimeters, or even just a few nanometers, across have a significant effect on the unfathomably large cosmos. It is the fundamental forces governing the behavior of atoms and molecules at this very minute level—such as their masses, how they interact with one another, and how they gain and lose energy—that drive the bulk properties of everyday objects.

- Chemists study the behavior and properties of atoms and molecules in a lab and then multiply what they observe by factors so astronomical that they are truly staggering. And when they do, they can often explain and even predict the behavior of macroscopic objects that affect our everyday lives.

- In the most remarkable cases, we have already employed this strategy to design new materials and medicines, and perhaps one day, we will even create life from nothing more than a few elements and our deep understanding of chemistry.

THE PERIODIC TABLE

- The periodic table—the most recognizable visual tool of chemistry—is a remarkable construct that organizes the most fundamental substances that make up our universe in a way that spatially demonstrates many trends in their properties.

- This table is not only 200 years in the making, but it encompasses thousands of years of human thought on the composition of matter. It is the pantheon of human understanding of the elements. But there is more than one way to organize these elements. In addition to the traditional organizational scheme, there are a few newer constructs that convey different types of information.

- Only about 100 elements are currently known to us, and even fewer of those form naturally. There are so many ways in which atoms can be combined that they create a huge library of materials with properties so varied that the possibilities are virtually limitless.

- To add to the complexity, there is more than one way to combine atoms together into molecules with what we commonly refer to as chemical bonds. It is the structure of atoms that allows us to predict and explain their bonding and, in turn, the bonding that helps us understand how molecules behave.

- The idea that all matter in the universe is composed of fundamental particles is pivotal to the development of chemistry, but it is not a new idea. Thinkers from civilizations as old as ancient Greece and China independently advanced the theory that there must be just a few basic materials that combine in various ratios to form all other materials.

- The philosopher Thales, who is widely credited with being the first philosopher to grapple with the concept of fundamental units of matter, offered the theory that all matter was created from just one fundamental substance: water. He suggested that this fundamental material took on various states—such as botanical, geological, meteorological, and so forth—and that combining these different forms of water created all of the material in the universe.

- But over time, other Greek philosophers began to find it difficult to believe that all complex materials were made of just one type of fundamental particle, and they began entertaining the notion that there might be more than one basic material. It was the only way to explain the remarkable diversity of the matter that they observed around themselves.

- Empedocles is famous for first postulating that there were 4 fundamental substances: earth, water, fire, and air. He called these fundamental substances elements and theorized that they combine in various ratios to make up all of the materials in the universe, and he seemed to be on to something. Having a library of just a few fundamental substances meant that they might be combined in various ratios to create a continuum of compositions, offering a buffet of materials that was virtually infinite.

- About a century later, famed thinker Aristotle theorized that Empedocles's elements had specific properties that could be used to organize them. He suggested that earth is cold and dry, water is cold and wet, fire is hot and dry, and air is hot and wet.

- Aristotle organized his elements spatially based on their properties, creating a graphical representation of the elements as he understood them, and his arrangement organized them by similarities and differences in specific properties. Even though this was first done with materials that are not actually elements, this simple idea of arranging elements based on their properties is the essence of the modern periodic table.

THE MODERN PERIODIC TABLE

- In the 1700s, Western scientific thought was beginning to awaken from the Dark Ages, and a looming industrial revolution was expanding the imaginations—and the bankrolls—of a whole new generation of European aristocrats. With all the time and resources needed for scientific investigation, these wealthy scientific pioneers stood poised to make a series of scientific breakthroughs that would change their world forever.

- One such aristocrat was Antoine Lavoisier, a French nobleman with a keen curiosity about the nature of matter. It was Lavoisier and his contemporaries who first began to chip away at the idea that water, air, earth, and fire are the fundamental elements of matter.

- For his part, Lavoisier did this by decomposing water in the presence of iron metal. Iron likes to rust, and the rusting of metal is a process in which the metal reacts to become what we call a metal oxide. When iron became iron oxide, snatching the oxygen from water, what remained was a gas made of what was left of the water molecules.

- Lavoisier demonstrated that he could collect this gas in a separate container and then burn it in air to regenerate water. He called this element hydrogen, meaning "water maker," because it could be burned in air to make water.

THE PERIODIC TABLE OF THE ELEMENTS

Hydrogen *** H 1.008 1																	Helium *** He 4.003 2
Lithium * Li 6.941 3	Beryllium * Be 9.012 4											Boron * B 10.81 5	Carbon * C 12.01 6	Nitrogen *** N 14.01 7	Oxygen *** O 16.00 8	Fluorine *** F 19.00 9	Neon *** Ne 20.18 10
Sodium * Na 22.99 11	Magnesium * Mg 24.31 12											Aluminium * Al 26.98 13	Silicon * Si 28.09 14	Phosphorus * P 30.97 15	Sulfur * S 32.07 16	Chlorine *** Cl 35.45 17	Argon *** Ar 39.95 18
Potassium * K 39.10 19	Calcium * Ca 40.08 20	Scandium * Sc 44.96 21	Titanium * Ti 47.87 22	Vanadium * V 50.94 23	Chromium * Cr 52.00 24	Manganese * Mn 54.94 25	Iron * Fe 55.84 26	Cobalt * Co 58.93 27	Nickel * Ni 58.69 28	Copper * Cu 63.55 29	Zinc * Zn 65.39 30	Gallium * Ga 69.72 31	Germanium * Ge 72.63 32	Arsenic * As 74.92 33	Selenium * Se 78.96 34	Bromine ** Br 79.90 35	Krypton *** Kr 83.80 36
Rubidium * Rb 85.47 37	Strontium * Sr 87.62 38	Yttrium * Y 88.91 39	Zirconium * Zr 91.22 40	Niobium * Nb 92.91 41	Molybdenum * Mo 95.94 42	Technetium * Tc [98] 43	Ruthenium * Ru 101.07 44	Rhodium * Rh 102.91 45	Palladium * Pd 106.42 46	Silver * Ag 107.87 47	Cadmium * Cd 112.41 48	Indium * In 114.82 49	Tin * Sn 118.71 50	Antimony * Sb 121.76 51	Tellurium * Te 127.60 52	Iodine * I 126.90 53	Xenon *** Xe 131.29 54
Caesium * Cs 132.91 55	Barium * Ba 137.33 56	LANTHANIDES	Hafnium * Hf 178.49 72	Tantalum * Ta 180.95 73	Tungsten * W 183.84 74	Rhenium * Re 186.21 75	Osmium * Os 190.23 76	Iridium * Ir 192.22 77	Platinum * Pt 195.08 78	Gold * Au 196.97 79	Mercury ** Hg 200.59 80	Thallium * Tl 204.38 81	Lead * Pb 207.2 82	Bismuth * Bi 208.98 83	Polonium * Po [209] 84	Astatine * At [210] 85	Radon *** Rn [222] 86
Francium * Fr [223] 87	Radium * Ra [226] 88	ACTINIDES	Rutherfordium **** Rf [267] 104	Dubnium **** Db [268] 105	Seaborgium **** Sg [269] 106	Bohrium **** Bh [270] 107	Hassium **** Hs [269] 108	Meitnerium **** Mt [278] 109	Darmstadtium **** Ds [281] 110	Roentgenium **** Rg [281] 111	Copernicium **** Cn [285] 112	Ununtrium **** Uut [286] 113	Flerovium **** Fl [289] 114	Ununpentium **** Uup [289] 115	Livermorium **** Lv [293] 116	Ununseptium **** Uus [294] 117	Ununoctium **** Uuo [294] 118

Lanthanum * La 138.91 57	Cerium * Ce 140.12 58	Praseodymium * Pr 140.91 59	Neodymium * Nd 144.24 60	Promethium * Pm [145] 61	Samarium * Sm 150.36 62	Europium * Eu 151.96 63	Gadolinium * Gd 157.25 64	Terbium * Tb 158.93 65	Dysprosium * Dy 162.50 66	Holmium * Ho 164.93 67	Erbium * Er 167.26 68	Thulium * Tm 168.93 69	Ytterbium * Yb 173.04 70	Lutetium * Lu 174.97 71
Actinium * Ac [227] 89	Thorium * Th 232.04 90	Protactinium * Pa 231.04 91	Uranium * U 238.03 92	Neptunium * Np [237] 93	Plutonium * Pu [244] 94	Americium * Am [243] 95	Curium * Cm [247] 96	Berkelium * Bk [247] 97	Californium * Cf [251] 98	Einsteinium * Es [252] 99	Fermium * Fm [257] 100	Mendelevium * Md [258] 101	Nobelium * No [259] 102	Lawrencium * Lr [262] 103

- Clearly, water must be made from simpler materials. By disassembling and then reassembling water, Lavoisier had effectively closed the book on the 2000-year-old paradigm that water was an element. Elements cannot be disassembled and reassembled, but water can.

- Lavoisier and others continued work in this vein, cataloging a few dozen of the elements we know today. In 1789, he famously published what is commonly regarded as the first modern chemistry textbook. His work contained a list of elements that had been discovered up to that point in time.

- A generation later, a German scientist named Johann Döbereiner reinspired the concept of organizing elements by their properties. In 1829, Döbereiner noted that known elements with very similar properties tended to group themselves into groups of 3. For example, lithium, sodium, and potassium are all soft metals that react readily with water to form very alkaline solutions. This property eventually led to them being dubbed alkali metals.

- He noticed that calcium, strontium, and barium all combine with oxygen in a one-to-one ratio and are commonly found in this state in nature, eventually earning them the classification of alkaline earth metals.

- A third example offered by Döbereiner was chlorine, bromine, and iodine. All of these elements are found naturally occurring as salts in combination with metals, such as the sodium chloride in table salt.

- But Döbereiner's triad model seemed to ignore a few relationships, such as beryllium and barium, which were known in his day to act like alkaline earth metals. It was also increasingly unable to explain the discovery of new elements, such as rubidium (in 1861) and cesium (in 1861), both of which seem to upset the triad model by behaving very similarly to lithium, sodium, and potassium.

- Another generation later, a Russian chemist named Dmitry Mendeleev played the same geometric game as Aristotle, but with 2 important differences: He had 63 accurately known elements to work with instead of Aristotle's mistaken 4, and he had the benefit of superior measurement techniques, which gave him the atomic masses of each element and a way to observe how they reacted with others.

- The genius that Mendeleev applied to this long list of elements was to arrange them in a grid based on their properties and known atomic masses. Mendeleev's grid-style table of the elements was so amazingly simple, accurate, and powerful that he was even able to predict the existence and properties of yet-undiscovered elements by searching for gaps in the patterns.

- The modern periodic table contains not only the 90 or so naturally occurring elements, but nearly 2 dozen more that have been created in laboratories around the world over the years. The legacy of researchers like Mendeleev and Lavoisier is alive even today as modern chemists and physicists have pushed the boundaries of nature itself, extending the catalog of elements beyond those found in nature in search of new manmade elements with yet-undiscovered properties.

- These newer elements give us great insight into the forces that hold atoms together and give them their characteristic properties, and with each new element discovered, we learn a little bit more about how the structure of the atom influences the properties of all matter in the cosmos.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 14–20, 25–29.
Gordin, *A Well-Ordered Thing.*
Morris, *The Last Sorcerers*, chap. 9.

QUESTIONS

1. What aspects of chemistry interest you the most?

2. What do you hope to learn about chemistry from this course?

Matter and Measurement

LECTURE 2

Atoms and molecules are substances that collectively make up practically every piece of matter that we will ever encounter but individually are so miniscule that they defy direct observation. In this lecture, you will discover how chemists deal with dramatically small—and large—numbers in measurement. You will learn about length and mass, 2 measurements that are so small in atoms that they defy conventional units. You also will learn how chemists count atoms and molecules and think about temperature. Finally, you will review issues of uncertainty in measurements.

SCIENTIFIC NOTATION

- Considering processes over huge differences in scale often leads to situations in which values spanning many orders of magnitude have to be compared. To cope with this, scientists use a special type of notation called scientific notation. Let's consider a few very simple numbers that differ widely in scale: a billion, a trillion, and a quadrillion.

- Each of these numbers has quite a few zeros after the 1. A billion is a 1 followed by 9 zeros, a trillion is a 1 followed by 12 zeros, and a quadrillion is a 1 followed by 15 zeros. Those zeros aren't doing much except conveying the size of the number.

- We can convey in a more compact fashion the number of zeros trailing these numbers by using an exponent: 1 billion becomes 1×10^9, where the 9 in the exponent conveys the number of zeros trailing the 1, in this case. Similarly, 1 trillion can be written as 1×10^{12}, and 1 quadrillion can be written as 1×10^{15}.

- This kind of treatment also extends to very small numbers—for example, a billionth, a trillionth, and a quadrillionth. These are very small decimals in which there are meaningful numbers at the end of the zeros, but there are long trails of zeros leading them that do nothing more than convey the magnitude of the number. To condense that magnitude into a simpler expression, we use negative exponents: 1 billionth becomes 1×10^{-9}, 1 trillionth becomes 1×10^{-12}, and 1 quadrillionth becomes 1×10^{-15}.

UNITS OF MEASUREMENT

- Scientific notation can help us by condensing the scale of large numbers down to an exponent, which makes it easier to look at, but it would be even more convenient if we could just use numbers that are manageable to begin with.

- Numbers are much more easily understood when they are reported in appropriate units. When scientific notation won't do, chemists have created new units of measurement that produce easily handled numbers on the scale of atoms and molecules.

LENGTH

- One of the simplest units of measurement is length. Measuring lengths or distances as accurately as possible is crucial in chemistry. When it comes to the positions of atoms in molecules, fractions of nanometers, or distances less than one-millionth the width of a human hair, it can make a difference.

- The metric system's standard unit of length is the meter. When we try to describe distances in atoms and molecules, meters lead to some pretty small numbers—so small that we don't ever really report these kinds of distances in meters. In fact, a typical atom is about 1×10^{-10} meters across.

- Scientific notation is one solution, but instead of working with awkwardly small numbers like this, we more typically use one of 2 strategies. First, we can use metric prefixes to pare down this meter close to the size of an atom: 10^{-10} meters becomes 10^{-7} millimeters, which equals 10^{-4} micrometers, which equals 0.1 nanometers, or 100 picometers. Finally, we are getting to a point at which the numbers we have to use to accompany the unit aren't so cumbersome.

- The second strategy is to create our own customized unit, tailored to be used in measuring distances at the atomic scale. Chemists have also done this, designating a length of 100 picometers, or 10^{-10} meters, as an angstrom, in honor of Anders Jonas Ångström.

- Using angstroms, the size of atoms and the bonds between them can be expressed in digits close to 1, simplifying the reporting process. A typical carbon-carbon bond, such as the ones helping to hold your DNA together, is about 1.5 angstroms long.

MASS

- Matter's defining characteristic is mass. All objects have mass—even atoms. But, just as we did with lengths, we run into a tough situation when it comes to reporting the mass of atoms and molecules. They are simply too small to use conventional units easily.

- Weight and mass are a very important pair of related properties. Larger objects, such as a person, can be weighed to obtain their mass. This is because Newton's law of gravitation tells us that the Earth pulls downward on us all with the same force, making our weight and mass proportional.

- But molecules and atoms are just too small for this kind of treatment. We can't weigh a single molecule or atom like we can larger objects.

- Chemists use a unit called the atomic mass unit (amu) to report on mass of atoms and molecules. As early as 1850, scientists were using this special unit to communicate the mass of a single atom of one type in comparison to another. Its original definition was 1⁄16th of the mass of a single oxygen atom.

- When you set the mass of an oxygen atom to 16, the mass of a hydrogen atom, the smallest atom, is equal to about 1. Oxygen was used as the standard simply because its natural abundance in our environment causes it to appear in so many naturally occurring materials. Hydrogen atoms are about 1 angstrom wide and have 1 atomic mass unit; oxygen atoms have 16 atomic mass units.

AMOUNTS

- In many situations, we measure collections of discrete objects not by their mass, but simply by the number of those objects present. For example, when atoms interact, bond, and undergo chemical processes, it is often in whole-number ratios of atoms, not their masses. So, many times it becomes critical to be able to report on a number of atoms in a certain sample, rather than the weights or mass of that sample.

- But this presents a real problem. Atoms are so small that chemists had to devise all new units of measurement just to report on their dimensions and mass without driving themselves crazy. So, once again, chemists have created their own counting unit, called a mole, which is 602 billion trillion, or 6.02×10^{23}.

- A mole is a difficult quantity to visualize. Because atoms are so very small, a mole is a very large number, thus allowing us to count atoms using numbers that don't boggle the mind. This famous number is commonly called Avogadro's number, in honor of Amedeo Avogadro who is often credited with first proposing the existence of such a proportionality, although he did not himself discover it.

TEMPERATURE

- Temperature is a measure of how hot or cold an object is. Early temperature measurements were conducted using the Fahrenheit scale, developed by German physicist Daniel Gabriel Fahrenheit in 1724. On Fahrenheit's scale, water freezes at 32° and boils at 212°. The exact references that he used to create his scale are a bit unclear, but it is generally presumed that he used the lowest obtainable freezing temperature of seawater as his reference point for 0 and human body temperature as his reference for 100.

- In 1742, however, Swedish physicist Anders Celsius proposed a slightly more systematic scale, using pure water as his reference material for both points, defining 0° as the freezing point of pure water and the boiling point of pure water as 100°. We often refer to his system as centigrade, indicating his 100° scale between references. Because each of these terms—"Celsius" and "centigrade"—both begin with the letter C, they have come to be used interchangeably.

- Both of these scales are fine for weather forecasting or a quick physical checkup from the doctor, but the temperatures that we experience on the surface of the Earth represent just a tiny fraction of the temperature conditions that the universe has to offer.

- To a chemist, temperature is a measure of the molecular motion in a system. It tells us how rapidly atoms and molecules move, collide, and even vibrate, twist, and tumble—which can help us understand why they behave the way they do.

- But if we want to explain how atoms and molecules behave throughout the universe, we have to consider all relevant temperatures that we might encounter—from the frigid conditions on the dark side of the Moon to the scorching center of a pulsar at the edge of the universe—and that requires us to rethink temperature a bit.

- We will need a scale of temperature that truly allows us to compare the atomic and molecular motions within any systems that we might encounter. It was nearly 100 years after Celsius that temperature scales got another upgrade—this time from William Thomson, Baron Kelvin, who proposed a new temperature standard.

- In Kelvin's time, it had been realized that atoms and molecules can move and collide and that their bonds can vibrate. These molecular motions are, essentially, temperature. The colder a molecule gets, the slower these processes become, and Kelvin wanted a temperature scale that directly communicated how vigorous these motions were in different environments.

- Kelvin suggested that the 0 reference of the centigrade temperature scale should be not the freezing point of water, but 273° below that—the temperature at which all molecular motion stops. This scale, in which the entire Celsius scale is offset by 273°, is called the Kelvin scale. We call the Kelvin scale an absolute temperature scale, because 0 Kelvins means no molecular motion, and you can't move slower than that. Kelvins are an indispensable unit of temperature in chemistry.

PRECISION AND ACCURACY OF MEASUREMENT

- In science, it isn't good enough to simply say whether a number is good or bad, reliable or unreliable. We need to carefully define what we mean when we describe the reliability of data, and we use 2 terms with very specific definitions.

- The terms "accuracy" and "precision" are thrown around quite a bit in popular media and casual conversation as synonyms meaning "of high certainty." But to scientists, these terms mean 2 very different, but equally important, things. We have to be very careful when using these terms, because to substitute one for the other can lead to serious miscommunications.

- Accuracy refers to the average value of a data set—how close it is to the actual value. Precision refers to how tightly grouped the individual data points are. Precision refers specifically to how reproducible individual readings are.

- Data sets can be accurate, but not precise. They can also be precise but not accurate. And they can be both accurate and precise. Precision only refers to reproducibility—not to accuracy—so a very precise measurement can in fact be wrong.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 14–20, 25–29.
Masterton and Hurley, *Chemistry*, 1.2–1.3.

QUESTIONS

1 Weight and mass are often used interchangeably in casual conversation, but they are in fact very different. Consider an object that weighs 2.2 pounds on the surface of the Earth and therefore has a mass of 1 kilogram. What are the weight and mass of the same object in deep space, where there is no measurable gravity acting on it?

2 Celsius (C) and Fahrenheit (F) scales both report on temperature, but each uses different reference points and scales for each degree. Knowing that 0°C and 32°F are equal values and that 1 degree Fahrenheit of temperature change corresponds to 5⁄9 of a degree in Celsius, how might one mathematically convert any temperature in degrees Celsius into degrees Fahrenheit?

Answer

2) $T_{(°C)} = (T_{(°F)} - 32) \times 5/9$.

Wave Nature of Light

LECTURE 3

We often rely on light to probe the properties of matter at the atomic and molecular level. Light interacts with atoms and molecules in specific ways, delivering and transporting energy that we can measure using devices as simple and familiar as the human eye or as complex and technical as a million-dollar electronic device. Because many of the techniques used by the modern chemist to characterize matter involve electromagnetic radiation—light—this lecture will introduce you to light from the perspective of a chemist.

WHAT IS LIGHT?

› Light is something so familiar to us that we often take it for granted. But what exactly *is* light? What is light made of? How does it move through space, and how does is carry energy? Is light simply a disturbance in matter, much like sound or seismic waves? Or is light actually matter—a stream of particles moving in a beam?

› These questions perplexed great thinkers as early as the time of ancient Greece, when Aristotle espoused one of the first theories on light, describing it as a disturbance in one of his proposed elements: air. This description makes some sense, because it is consistent with light being a wave, which we know from experience moves and carries energy.

› Around the same time, Democritus, another Greek philosopher, posited that light might instead consist of small, indivisible particles like atoms, but with an identity and makeup all their own. This idea also makes sense—a stream of particles moves and carries energy with it.

- Although both of these theories about the nature of light would seem to explain its ability to carry energy as it moves through space, they also appear to be diametrically opposed. It seems that light has to be one or the other—a wave or a stream of particles. Neither Aristotle nor Democritus had the technology necessary to test their theories scientifically, leaving the true nature of light as a matter of debate in their time.

- Even as Europe was exiting the Dark Ages, Isaac Newton and his contemporaries struggled with defining what makes up light. Newton's famous corpuscular theory sided with Democritus, offering that only particles could be refracted by a prism, which he used to observe the visible spectrum.

- But another famous scientist of the time, Christiaan Huygens, countered Newton's theory by suggesting that the same phenomenon could be explained as waves propagating at different speeds through 2 different media—in this case, air and quartz.

- The debate over the particle or wave nature of light only started to come to a resolution in 1803, when a remarkably simple but scientifically sound experiment produced a result that confirmed that light propagates in waves.

THE WAVE NATURE OF LIGHT

- English physicist Thomas Young grew up studying the work of the incomparable Isaac Newton. Young had a great deal of respect for Newton's work, but he wasn't buying Newton's corpuscular theory of light, and as a young researcher, he set out to disprove it.

- Young made many contributions to the science of physics, but arguably his greatest is an experiment that proved indisputably that light consisted of waves. In addition, it was such a simple and elegant proof that it could be verified by anyone using household items and sunlight.

- In Young's famous double-slit experiment, when light is passed through 2 slits, multiple bands of light result. These bands form because as light waves pass through the slits, they radiate outward from them. This creates a pattern of interference in which waves generated at different slits occasionally interfere constructively with one another, creating a fanned-out pattern of light bands.

- If a stream of particles were passing through the slits instead, the beam would simply be divided into 2 smaller, parallel beams of light.

- Young's experiment provided proof that light must be wave-based. And because it is a wave, light has all the same characteristics as any other wave, such as wavelength, velocity, frequency, and wave number. We can measure these characteristics and classify light based on them.

THE ELECTROMAGNETIC SPECTRUM

- Isaac Newton handily proved that light could be separated by passing it through a prism at the appropriate angle. When he did this, he demonstrated that what we commonly call white light is actually a collection of many different colors of light. Newton coined the term "spectrum" to describe this collection of different-colored lights.

- Scientists today know that these different-colored lights are the result of slight variations in their wavelengths. In the case of visible light, we are talking about wavelengths of about 400 to 800 nanometers.

- "Light" is a term that most of us use to describe electromagnetic radiation that our eyes can detect. In truth, we would be talking about visible light in a situation like this. Our eyes are a remarkable product of evolution, but they have their limitations. In this case, it turns out to be a pretty severe limitation.

- In 1800, an English researcher named Sir William Herschel discovered that prisms separate not only visible light, but an invisible form of light that falls beyond the red end of the spectrum. He named this infrared because of its location past the red.

- A year later, in 1801, Johann Wilhelm Ritter discovered another invisible form of light capable of darkening silver salts. Because this type of light fell outside of the blue, or violet, end of the visible spectrum, Ritter called this ultraviolet light.

- Light comes in many more forms than that which we can see with the unaided human eye. Even Herschel and Ritter could not possibly have guessed just how far outside of the visible spectrum light goes. It is staggering.

- Thanks to Young's experiment, we know that all light is made up of electromagnetic waves, so we characterize each region of the spectrum based on the wavelength of light that produces it. These wavelengths can span a remarkable range of distances.

- When we line up all possible wavelengths from shortest to longest, we get what is commonly called the electromagnetic spectrum.

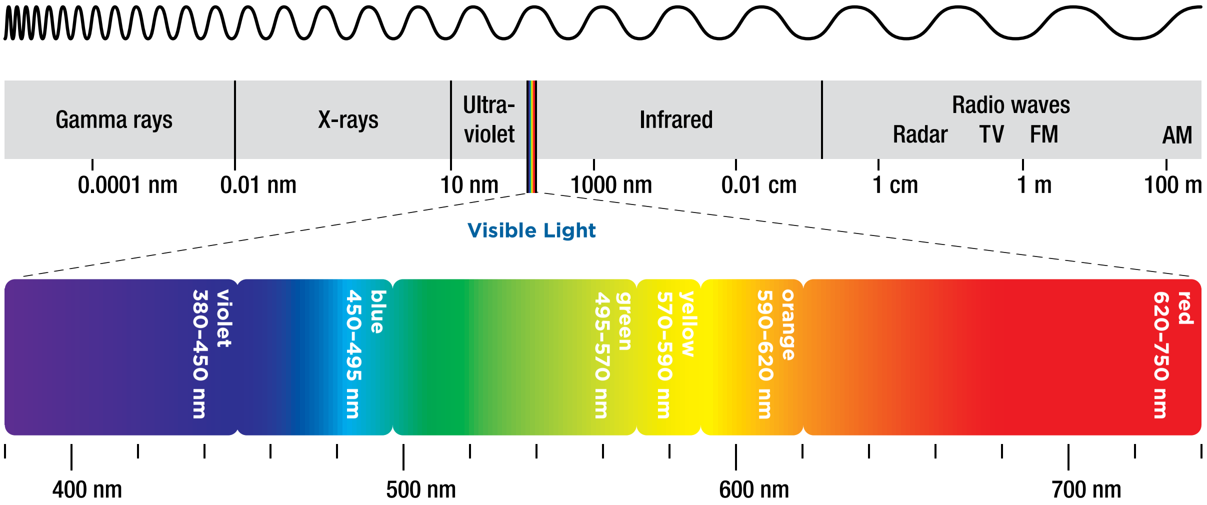
- At the extremely short-wavelength end of the electromagnetic spectrum are gamma rays. These extremely high-energy rays have wavelengths so small that they are even smaller than atoms.

- Next in line are X-rays—light with a wavelength just about equal to the size of an atom. X-rays have the ability to expose photographic film just like visible light, but X-rays carry so much energy that they can penetrate flesh, but not bone. This has led to their use in medical imaging, and the former property has allowed many researchers to use them as a scientific tool.

- Next is ultraviolet radiation. Wavelengths of ultraviolet light tend to be near the size of many molecules. They are just about 100 nanometers across.

- Next is visible light—that small slice of the electromagnetic spectrum that we use every day to observe our world through our eyes.

THE ELECTROMAGNETIC SPECTRUM



- A slight increase in the wavelength again takes us into the infrared region of the spectrum. Infrared radiation is emitted by matter naturally around the temperatures that we experience on the surface of the Earth. This makes them interesting from a number of potential applications, not the least of which is being able to detect the presence of warm objects in what we perceive to be complete darkness.

- Next comes microwave radiation, which has wavelengths around 1 meter. Microwaves have always been fascinating to scientists, but in recent decades have become best known for their use in exciting water molecules to generate heat in the form of microwave ovens.

- After microwaves are radio waves—waves so long that their wavelengths can easily span distances of miles. The most familiar technology associated with radio waves is the transmission of audio information, but just as with all other forms of radiation, radio waves have other properties and applications exploited by chemists to help us understand the world around us.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 218–220.

UC Davis ChemWiki, “Wave-Particle Duality.”
http://chemwiki.ucdavis.edu/Core/Physical_Chemistry/Quantum_Mechanics/02._Fundamental_Concepts_of_Quantum_Mechanics/Wave-Particle_Duality.

QUESTIONS

1 Scientific instruments sometimes use diffraction gratings to separate various wavelengths of light from a single beam. If a beam of light containing all visible colors were passed through a double slit, like in the demonstration from this lecture, what would the light pattern look like?

2 In 2015, a research team built the smallest-wavelength laser ever created by humans. It produces a light beam with a frequency of 2.0×10^{18} hertz. What is the wavelength of this light, and how does it compare to the diameter of a hydrogen atom (about 0.12 nanometers)?

Answer

2) 0.15 nanometers (nearly the same size as a hydrogen atom!).

Particle Nature of Light

LECTURE 4

Thomas Young's double-slit experiment provided compelling evidence that light was a wave, and 2 centuries of scientific investigation have relied on our understanding of the wave properties of light. But, as you will learn in this lecture, a simple observation and a sharp mind started the process of questioning what we thought we knew for certain. Heinrich Hertz discovered the particle nature of light and how light's ability to carry discrete packets of energy can be demonstrated using the photoelectric effect. Then, Albert Einstein postulated that light was something very special that shared properties of both waves and particles. Finally, Louis de Broglie discovered that all moving particles have duality.

DUALITY AND THE PARTICLE NATURE OF LIGHT

- Heinrich Hertz was a German physicist and is the namesake for the hertz unit that we use today to describe the frequency of electromagnetic radiation. One of Hertz's groundbreaking observations came in 1887, when he developed a device that could generate a spark in the presence of light. Simply by exposing metal to light, he was able to generate an electrical current. But there was a curious twist to Hertz's experiment.

- What did Hertz see in his own experiment that made him question such an elegant result as the one that Thomas Young had produced in his double-slit experiment? Hertz saw the photoelectric effect, which predicts that when light of a certain energy strikes metal, the electrons in the metal atoms are promoted into what is called the valence band and can then move along the metal as an electrical current, dissipating the charge.

- Hertz demonstrated that light transmits energy in packets of energy—just like objects. Therefore, light must be a particle. This is the opposite of what Young had discovered: that light was a wave.

- Hertz's experiment showed that there was no effect when the light's wavelength was increased—not a smaller effect as one might predict simply based on the fact that a longer-wavelength light carries less energy. This is a serious problem for advocates of the wave theory of light. In situations like these, light is acting less like a wave and more like a beam of particles, each of which carries a very specific packet of energy. The photoelectric effect wasn't attenuated or decreased when the energy in the light was lowered—it stopped.

- Hertz failed to immediately recognize how profound his observations were, and we were forced to wait for the great minds of the early 1900s, such as Max Planck and Albert Einstein, to begin to understand why the photoelectric effect seems to support that light is a particle.

- The only possible explanation for Hertz's results is that light consists of particles that carry discrete packets of energy. The truth is that light behaves both ways—sometimes like a particle, but in other ways like a wave. Light requires us to think about how matter and energy move in a whole new way, blending the characteristics of waves and particles. This remarkable property is often called the duality of light.

PHOTONS AND QUANTUM THEORY

- So, light suffers from an identity crisis, having characteristics of both waves of electromagnetic energy and of particles carrying defined packets of energy. But exactly how much energy is in one of these packets? How do we tie the duality together?

- In 1900, German physicist Max Planck determined a physical constant that he called the quantum of action, which is represented by h and has a value of 6.63×10^{-34} joule-seconds. This constant was first developed by Planck in an attempt to explain why light seemed to only be emitted from objects in fundamental packets of energy called quanta.

- But it took the mind of an upstart young scientist to find the most profound application of Planck's constant. In 1905, the incomparable, but yet-unheard-of, Albert Einstein published a flurry of papers on the topic of relativity and quantum physics. In these papers, he laid the groundwork for a discussion that would shed light on the true nature of electromagnetic radiation.

- Einstein's genius was to point out that Planck's equation could only be reconciled if light had particle character. It might seem obvious to us now, but in his day, it took a tremendous leap of logic to consider that the wave characteristics observed by Young didn't necessarily mean that light can't also be treated as a particle.

- These particles of light are called photons, and using Planck's constant, we can calculate the amount of energy carried by a photon of any type of light simply based on its frequency, and vice versa, by using the following equation: $E = (hc)/\lambda$, where E is energy, h is Planck's constant, c is the speed of light, and λ is the wavelength.

- This equation unifies the wave and particle theories of light in a single equation, allowing scientists to switch back and forth from one to the other as necessary to explain their observations.

DE BROGLIE WAVELENGTHS

- It is a bit shocking to realize that small, fast-moving photons can have properties of both waves and particles. But another shocking piece of information is that photons aren't alone in their identity crisis.

- In 1923, a French graduate student named Louis de Broglie forwarded a simple but revolutionary hypothesis. He suggested that any moving particle—anything from the tiniest subatomic particles to planetary bodies—had an associated wavelength.

- He used the example of a relatively fast light particle called the electron. This particle is thousands of times less massive than any atom, but it is much more massive than a photon. In the 1920s, everyone was quite sure that electrons were particles. The charge and mass of a single electron had been measured to great accuracy, and both of these properties could only belong to particles.

- De Broglie suggested that as particles became larger and slower, their momentum—that is, their mass times their velocity—could be used to describe their wave behavior. He derived the following equation: $\lambda = h/p$, where λ is wavelength, h is Planck's constant, and p is momentum. De Broglie found that this equation described the wave behavior of the electron perfectly, too. He had proven that wave-particle duality was not limited to photons.

- But if this is so, then why aren't we all well aware of this duality from our everyday lives? If a basketball on its way to the hoop has momentum, then it should have a wavelength, too—and so should a car barreling down the road, and even planet Earth as it makes its way around the Sun.

- The reason is that when we calculate the de Broglie wavelengths for these larger, slower-moving objects, we find wavelengths so incredibly small that they defy observation. The de Broglie wavelength for a high-speed electron—one moving about $1/50$th the speed of light—is about 100 picometers, which is just about the width of an atom.

- But consider some larger, slower-moving objects, such as a baseball on its way from a pitcher's mound to home plate, or even planet Earth. For example, that baseball has a de Broglie wavelength of about 10^{-34} meters, a distance so vanishingly small that it defies comparison to anything material. That distance is a trillionth of a trillionth of a 10 billionth of a meter.

- As another example, Earth, careening through space at 30,000 meters per second, has a de Broglie wavelength of 4×10^{-63} meters, which is 30 orders of magnitude smaller than the already-miniscule wavelength of the baseball example.

- Nonetheless, de Broglie's ingenious hypothesis proved true in the case of electrons, which are small enough and fast enough that their wave behavior is observable. By showing that the duality of light was the rule, not an exception to the rule, he cemented the concept of wave-particle duality in the minds of physicists and chemists that would follow him. And this is a good thing, because understanding the wave nature of electrons played a crucial role in unraveling the structure of the atom itself.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 220–223, 228–231.

UC Davis ChemWiki, "Quantum Mechanics."
http://chemwiki.ucdavis.edu/Core/Physical_Chemistry/Quantum_Mechanics.

QUESTIONS

1. If the corpuscular theory, or particle nature, of light is at least partially correct, then is it safe to assume that photons are massless as we so often do?

2. The human eye perceives water as being colorless, meaning that it does not absorb visible light. However, water does absorb light with a wavelength of about 2700 nanometers. How much energy is contained in a single photon of this type of light? In which part of the electromagnetic spectrum does it lie?

Answer

2) 7.4×10^{-20} joules. This is in the infrared region of the electromagnetic spectrum.

Basic Structure of the Atom

LECTURE 5

Atoms are comprised of 3 types of particles called subatomic particles: positively charged protons, negatively charged electrons, and neutrons, which have no charge. Protons and neutrons are of nearly equal mass and reside in a dense nucleus at the center of the atom. But much smaller, negatively charged electrons orbit this nucleus, balancing out the positive charge provided by the protons. In this lecture, you will learn how each of these particles was discovered and how the culmination of generations of scientific work ultimately came together to create our understanding of the most fundamental unit of matter: the atom.

ORIGINS OF ATOMIC THEORY

- The notion of atoms was first forwarded by ancient Greek philosophers who postulated that there are just a handful of fundamental substances that combine in various ways to form all others. The Greeks widely believed these elements to be air, water, earth, and fire—and they also believed that particles of these elements were absolutely indivisible.

- Today, we know that none of these are actually elements, and we also know that atoms of true elements can in fact be divided, but that they change to a new element when they are. Nonetheless, the Greek term "atom," meaning "not divisible," has stuck and is still how we refer to the smallest quantity of a given element that can exist.

DALTON'S ATOMIC THEORY

- Discourse over the nature of matter and its fundamental units slowed to nearly a halt with the fall of ancient Greece, and it wasn't until the start of the 19th century that the concept of the atom was revived, primarily as a result of the work of John Dalton. Dalton didn't have the sophisticated scientific instrumentation that we do today, so he had no way to see or experiment directly with atoms. What he did have, though, was a keen intellect and the benefit of the work of Antoine Lavoisier and others.

- Using relatively simple observations, Dalton was able to formulate a sound atomic theory. He found that when 2 elements combine to form a compound, the mass of all the products is equal to the masses of all the starting materials. This is the law of conservation of mass.

- He also found that when 2 elements combine to form more than one compound, the weights of one of the elements that combine with a fixed weight of the other are in a ratio of very simple whole numbers. This is the law of multiple proportions.

- It's the combination of these 2 laws that gave Dalton an airtight argument for the existence of indivisible atoms that come together in these simple whole-number ratios to create molecules.

- But Dalton had no way to effectively probe the structures of his proposed atoms. His observations proved their existence, but they could not explain exactly what atoms themselves were made of. We would have to wait another century before technology caught up with the atom, giving us a way to learn the inner workings of this remarkable construct of nature.

DISCOVERY OF THE ELECTRON

- The first of these advances is the cathode-ray tube, which was developed at the end of the 19th century and was used in televisions up until a decade ago. Cathode-ray tubes played an important role in the advancement of human understanding of atoms.

- Using the cathode-ray tube, J. J. Thomson was able to create isolated beams of pure electrons, measuring their mass, velocity, and charge. Thomson's measurements led him to a startling conclusion: that electrons were much smaller than atoms.

- This led Thomson to propose the first structural model for an atom. More than 100 years after Dalton repopularized the concept of atoms, the first attempt to explain their structure had finally been offered. Thomson postulated that atoms consisted of the small, negatively charged electrons he had observed—embedded in a very low-density, positively charged, spherical matrix making up the rest of its mass.

- A sketch of this model, with electrons peppered onto a positively charged sphere, evokes images of raisins in a bowl of pudding, earning it the moniker of Thomson's plum pudding model.

- But this first attempt to explain atomic structure was short-lived, because less than 2 decades after Thomson proposed the plum pudding model, his protégé, Ernest Rutherford, conducted an experiment that intended to build on Thomson's model, but instead disproved it.

THOMSON'S PLUM PUDDING MODEL

DISCOVERY OF THE PROTON

- Rutherford is credited with the discovery of what are known as alpha particles, which are much larger charged particles (more than 1000 times larger than electrons) created during the radioactive decay of uranium. But Rutherford is most famous not for discovering these particles, but for what he did with them next.

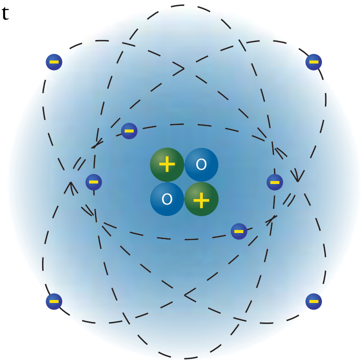
- Rutherford was curious to know how these relatively large, energetic particles would interact with atoms as they passed through a thin foil, so he pointed a beam of alpha particles at a piece of gold foil, encircling the foil in a special fluorescent screen that would light up when struck with an alpha particle. Assuming that Thomson's model was correct, the alpha particles were expected to simply pass through the foil, being scattered only slightly, if at all.

- As the experiment progressed, he noted that the brightest spot was directly behind the gold foil, just as he had expected. But Rutherford was stunned when he turned his attention to the other side of the screen and saw that a few particles were deflected almost directly back toward the source.

- Clearly, Thomson's model was not correct. If the mass of gold atoms was distributed across their entire volume, then there is no way that an alpha particle could be reflected back toward the source.

- Rutherford's results strongly indicated that atoms were made of mostly empty space, with a highly concentrated nucleus containing most of its mass in just a small fraction of the atom's total volume. This would explain why, on rare occasion, an alpha particle bounced back. Only an extremely dense point of matter taking up a small volume of the atom's total could possibly withstand the impact of an alpha particle and cause it to ricochet back in its original direction.

- So, there had to be an extraordinarily dense, but vanishingly small, point of mass at the center of atoms. Rutherford realized, then, that atoms were mostly made of empty space with a dense point of mass at their center. His model that accounts for this has been dubbed the Rutherford model, sometimes also called the nuclear model, because it is the first to acknowledge that most of the atom's mass resides in a small, dense nucleus at its center.



THE RUTHERFORD MODEL

- Rutherford had discovered that atoms consisted of a dense, positively charged nucleus surrounded by very light, negatively charged electrons. While atoms have diameters of around 100 picometers, or about one-tenth of a nanometer, Rutherford's work eventually led to the discovery that the radius of a typical nucleus is only about 1⁄100,000th that of its electron cloud—that is, 1 femtometer, or 0.000001 nanometers.

- Rutherford had determined that massive, positively charged particles were concentrated in the nucleus of the atom. Protons had been discovered.

DISCOVERY OF THE NEUTRON

- As research on radioactivity continued, there were some observations about atomic nuclei that weren't adding up. Specifically, researchers had irradiated beryllium with alpha particles to produce a new kind of radiation—one that didn't bounce off of nuclei like Rutherford's alpha particles, but instead crashed into them with force, knocking protons out of target atoms.

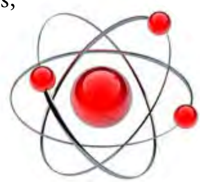
- The final key to understanding these unusual observations came in 1932, when James Chadwick, formerly a student of one of Rutherford's assistants, completed the inventory of subatomic particles. Chadwick reasoned that the radiation from beryllium was able to penetrate other atomic nuclei better because it was uncharged.

- Whereas the alpha particles used by Rutherford carried positive charge and were repelled by the positive nuclei of atoms they struck, sending them back, these new particles, though massive, must be uncharged.

- The lack of an electrostatic repulsion allowed these new particles to strike other nuclei with great force—a force that Chadwick used to estimate the mass of one of these new particles, which he called neutrons. Not surprisingly, they were just a fraction of a percent larger than protons.

- Because protons and neutrons are so similar in mass and contribute nearly all of the mass of an atom, chemists use a unit of mass called the atomic mass unit (amu) to compare the masses of atoms to one another.

STRUCTURE OF THE ATOM



- By 1932, the combined thought of the ancient Greeks, Dalton, Thomson, Rutherford, Chadwick, and many others had led us to an understanding of an atomic structure that looks something like what we see today in popular depictions of the atom.

- All atoms consist of a dense central core of matter, called the nucleus. In that nucleus are one or more protons. In the case of hydrogen, there is just one. An atom of the element hydrogen is the simplest atom.

- Around that dense, positively charged core are electrons. In the case of hydrogen, there is just one electron to balance the positive charge from the proton in the nucleus. This is a complete hydrogen atom with a nucleus and an electron cloud around it. We sometimes refer to this version of hydrogen as protium, because its nucleus contains just a single proton.

- The proton count in the nucleus is what gives elements their identity, so we can add a neutron to the hydrogen atom and still have hydrogen. But this makes the hydrogen atom about twice its original mass. We call this type of hydrogen—one in which a neutron is also present, making it more massive—deuterium.

- We can increase the mass of the hydrogen atom again by adding another neutron to get tritium—another form of hydrogen that is 3 times the mass of its simplest form. All 3 of these atoms are hydrogen, but they are different by way of their masses. We call these atoms isotopes of one another.

- If we add another proton to the atom's nucleus and another electron to its cloud to balance out the charge, we now have a new element, because the number of protons in the nucleus has changed.

- We can estimate the atomic mass of an elemental isotope simply by adding up the number of protons and neutrons in the particular isotope.

- There are many elements that exist in nature as 2 or more isotopes. In fact, most of them do. When this is the case, the periodic table reports the average mass of a given element in nature.

FORMATION OF IONS

- When the number of protons and electrons are out of balance, we create a species that carries a net overall charge. These charged species can have properties that are drastically different than their corresponding neutral atoms.

- These charged atoms are called ions. In general, if there are excess electrons, we get a negatively charged ion called an anion. If there is instead an excess of protons, we get a positively charged ion called a cation.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 37–48.
Masterton and Hurley, *Chemistry*, 2.1–2.2.
Morris, *The Last Sorcerers*, chap. 7.

QUESTIONS

1 If negatively charged electrons are attracted to positively charged atomic nuclei, what keeps the electron cloud of an atom or ion from collapsing?

2 How many neutrons, protons, and electrons are in the following atoms and ions?

a An atom of plutonium 244

b An oxide ion (O^{2-}) made from oxygen's most abundant isotope

Answers

2a) 94 protons, 150 neutrons, 94 electrons;
2b) 8 protons, 8 neutrons, 10 electrons.

Electronic Structure of the Atom

LECTURE 6

The cloud of electrons around a nucleus contains a very complex system of electron orbits, and the position of the electrons within the cloud of an atom or ion is one of the most significant driving factors in how these elements behave. This lecture will investigate the electronic structure of the atom. As you will learn, the size, shape, and orientation of an electron's orbit in conjunction with the electron's magnetic spin make every electron in an atom distinct from all others in that same atom.

BOHR'S MODEL

- Ernest Rutherford was able to demonstrate that atoms consisted of dense, positively charged nuclei with sparse electron clouds around them. But the Rutherford model had those electrons awash in a symmetrical, spherical sea of space, swirling around the minute nucleus and held in place by electrostatic attraction. Each electron was indistinguishable from the others, their only job being to balance the strong positive charge at the center of the atom.

- Rutherford, J. J. Thomson, and James Chadwick made indispensable contributions to our understanding of the subatomic particles making up the structure of the atom. But the story of the atom's structure isn't yet complete. It turns out that electron clouds take on a structure much more complex than any of these men had imagined.

- The key to demonstrating how complex electron clouds really are had already been developed several years before Rutherford's experiment by a French chemist and businessman named Georges Claude, who had started a successful company that liquefied air as a means of isolating commonly used and abundant atmospheric gases like nitrogen and oxygen.

- One of the by-products of this process is a small amount of neon, which is harmless and nontoxic, so Claude could have easily treated it as a waste product of his process. But a curious Claude decided to study these gases, rather than discard them. During his tinkering, he noticed that when a current was passed through a pure sample of neon gas enclosed in a glass tube, the gas glowed with an intense, pleasing light. It did not glow white, but a beautiful and distinctive hue of orange.

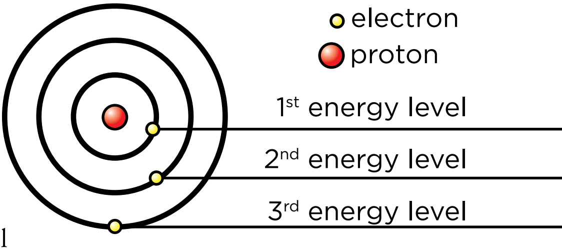
- There was clearly no chemical reaction taking place, because neon is an inert gas, so the source of the electromagnetic radiation causing the light had to be the result of some change in the neon atoms as electricity passed through them.

- Even more tantalizing, when Claude replaced the gas in his lights with another inert gas called argon, he instead obtained a white glow. Mixing the gases contained in the tubes produced lights of varying colors, creating a versatile and eye-catching product.

- It was just shortly after the invention of the neon light, in 1913, that Niels Bohr, a Danish physicist, offered a theory about the atom that explained this phenomenon and completed the modern understanding of atomic structure.

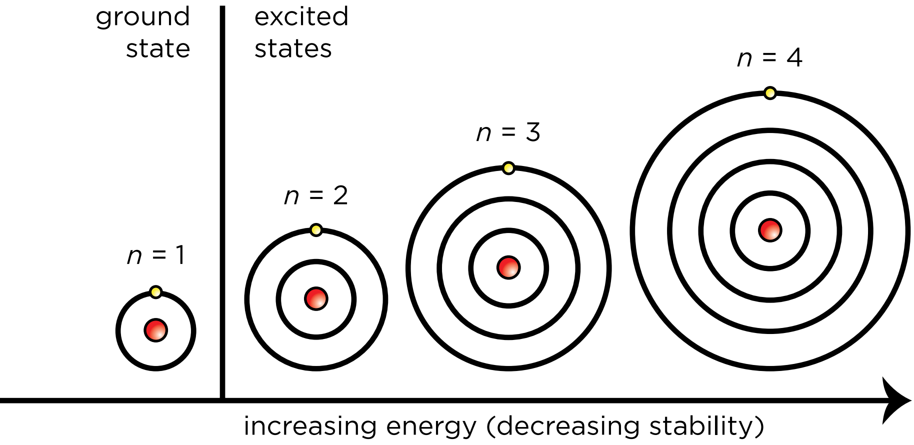
- Bohr theorized that the electrons in atoms do not simply orbit at random distances to the nucleus, but instead that they are constrained to more specific regions of space around it, which he called energy levels. Electrons could transition from one energy level to the other but could never lie in between the 2.

- Essentially, Bohr argued that electron orbits are like steps on a ladder. As you climb a ladder, you input energy obtained from burning calories from your breakfast. That energy becomes stored in the system as what is called potential energy. But your feet can only reside at specific, discrete distances from the ground. If you try to rest your foot between any 2 of these levels, you can't. Only certain, discrete amounts of energy can be put into the system.



- If you move up by one rung on the ladder, your physical potential energy increases. In other words, each time you step up to a new, higher rung, your somewhat unpleasant trip down will result in a greater force at impact, because all that stored potential energy is released. But the fall scenarios are not a continuum of forces; there are just a few discrete forces that you might experience—the experience corresponding to falling from the first rung, falling from the second, etc.

- Just as the ladder has discrete levels on which you can stand, the electron cloud of an atom has specific levels—in this case, orbits—in which an electron can reside. Use electricity or heat to move the electron into a higher energy orbit and its potential energy increases. Allow the electron



to fall down to a lower energy orbit and its potential energy decreases. But this time, the energy is emitted not as heat, friction, sound, and broken bones, but as a photon of light.

- Bohr's new model could explain the phenomenon of neon lamps. Electricity promotes an electron to a higher energy level in an atom, where it can then fall back downward, emitting light when it does, but only in very specific, defined packets of energy corresponding to very specific colors of light.

GEOMETRIES OF ATOMIC ORBITALS

- Bohr's model was a huge leap forward in understanding atomic structure. It was very close to the truth—but just a bit too simple. Bohr established that the electrons in an atom's electron cloud are not in random motion around the nucleus, but that they occupy very specific regions of space. Bohr's refinement to the model of the atom was to treat electrons like planets in a solar system, occupying only certain orbits around the central star.

- But there is one last refinement that we have to make to get our model of the atom into the modern age. The final piece of the electron puzzle was theorized by Erwin Schrödinger, an Austrian physicist.

- In the aftermath of Albert Einstein's groundbreaking theory about the duality of light, Schrödinger began to wonder whether electrons could also have dual properties. Might they also in some ways behave like waves instead of particles?

- When Schrödinger applied his idea to the structure of the atom, he realized that electrons don't move in circular orbits the way a particle or a planet might. Rather, they can occupy some very unusually shaped regions of space that make sense when you think of electrons as waves.

- Although this theory was a departure from the idea that electrons followed circular orbits around a nucleus, Bohr's original ideas and the similarities to the orbits of physical objects have led these regions of space occupied by electrons to be called orbitals.

- Chemists have characterized these orbitals, each of which is distinct from all others in the atom in one way or another. Exactly which orbitals do or do not contain electrons in an atom can give that atom many of its properties. There is an address for each electron in the atom that allows us to discuss just one electron or type of electron when it is warranted.

- Four distinct properties of the orbiting electron are needed to convey its address: the orbital's size, shape, and orientation, as well as a special property of the electron itself known as spin.

- The first of these properties is the size of the orbital, which is indicated by the principal energy level. For example, orbitals in the first principal energy level are generally smaller than those in the second, which are themselves smaller than the third.

- The next is the shape of the orbital. We indicate shapes by referring to what is called a subshell. Each principal energy level has a number of subshells equal to its principal number. For example, the first principal energy level has one subshell. The second principal energy level has 2 subshells. The third has 3, and so on.

- The first subshell of any level is called the *s* subshell. *S* subshells are spherical, so they contain only one orbital each. The second subshell is called the *p* subshell, and it contains 3 orbitals shaped like a dumbbell centered around the nucleus. The third subshell contains 5 *d* orbitals of more complex geometries, and the fourth subshell contains 7 *f* orbitals, whose geometries are truly perplexing to the uninitiated.

- Nonetheless, because each orbital within a specific subshell has similar shape and size, electrons that occupy them will have the same stability. Sets of orbitals with the same stability are called degenerate orbitals.

- Next we come to the third property: the orientation of the orbital. There is only one *s* orbital per energy level because a sphere centered on the nucleus can only have one orientation. But the *p* subshell contains

3 dumbbell-shaped orbitals, and each orbital has its own axis that is arranged perpendicular to the other 2, like the axes on a Cartesian coordinate. So, we often refer to these as the *px*, *py*, and *pz* orbitals.

- The final parameter is a magnetic property of the electron itself called electron spin. Any electron in an atom can have one of 2 magnetic alignments. Physicists call these 2 alignments spin up and spin down. Sometimes you might see them written as +½ and –½.

- It is because of this magnetic spin that 2 electrons can occupy the same orbital. Electrons usually like to have their space. They push against one another because they have like charges, and packing 2 negatively charged particles in the same orbital creates a repulsive force, which makes it energetically unfavorable to do so.

- But in certain situations, electrons of opposing spin can share an orbital, because having their magnetic spins aligned in opposing directions creates a small attractive force that does not fully cancel out their electrostatic repulsion, but does lower it somewhat. So, electrons often occupy orbitals in pairs, one spin up and one spin down.

QUANTUM NUMBERS

- Each electron has its own home in space around the nucleus. To communicate that location, we need an address—and that is exactly what Schrödinger proposed. Schrodinger's system of quantum numbers gives us a way to refer to a single, specific electron within an atom, facilitating the discussion about the electronic structure of the atom.

- Each atom has dozens of available atomic orbitals into which its electrons can go. Where can we expect to find the electrons in any given atom? Most often we discuss the electronic structure of atoms in what is called the ground state, which is simply the most stable arrangement of electrons possible.

- Let's say that we have an atom with no electrons in its cloud and our job is to fill that cloud with electrons in its ground state configuration. When we limit our discussion to the ground state of an atom, it turns out that electrons fill atomic orbitals in a very predictable way. To do this, we need to first set 3 important rules for the filling of orbitals within the electron cloud:
  1. There is a very specific filling order for orbitals in an electron cloud. This order is called the Aufbau order, from the German word meaning "building up."

  2. Hund's rule states that electrons will spread out within a specific subshell, placing one electron in each degenerate orbital before any electrons in that subshell pair up. Electrons like their space, and given the option to have an orbital of the same energy all to themselves, they will take that orbital.

  3. The Pauli exclusion principle states that no 2 electrons can have the exact same orbital address and spin state. In other words, no 2 electrons in the same atom can have the same 4 quantum numbers.

- Just as the state, city, street, and house number allow us to unambiguously define a location on a map, we need to quickly and easily define the energy level, subshell, specific orbital, and spin of a given electron to define its location within the electron cloud.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 224–228, 231–249.
Masterton and Hurley, *Chemistry*, 6.1–6.6.
Morris, *The Last Sorcerers*, chap. 10.

QUESTIONS

1. Thermally or electrically exciting an atom can promote one or more of its electrons to a higher energy orbital, placing the atom in what is called an excited state. Is this excited state a violation of either Hund's rule or the Pauli exclusion principle?

2. Are all emissions from excited atoms and ions necessarily visible to the human eye?

3. How many electrons are in the fourth energy level of gallium (Ga) in its ground state? What are the principle and azimuthal quantum numbers for the highest energy electron in that atom?

Answer

3) There are 3 electrons in the fourth energy level of gallium ([Ar]$4s^2 3d^{10} 4p^1$). The principle and azimuthal quantum numbers for the $4p$ electron are $n = 4$, $l = 2$.

Periodic Trends: Navigating the Table

LECTURE 7

Dmitry Mendeleev's original method of listing elements in the periodic table, by atomic mass, was a happy accident. In truth, the atomic number—the number of protons in the nucleus of an element—is used as the criterion for the ordering. The modern periodic table arranges elements spatially based on their atomic structures, creating a graphical tool that arranges the elements in a way that helps us predict and understand their properties. In this lecture, you will explore a few of the most fundamental trends in elemental properties that are revealed by the periodic table.

AN ATOMIC PERSPECTIVE ON THE PERIODIC TABLE

- The most obvious organizational feature of the periodic table is that elements become larger and larger as we read across the table from left to right, just as Mendeleev noted. But the modern table uses not the atomic mass of each element as Mendeleev did, but rather its atomic number—the number of protons in an element's nucleus.

- It was a fortunate coincidence for Mendeleev that as the number of protons in an element increases, so do the total number of nucleons, including neutrons, meaning that atomic mass and atomic number follow the same trend. We now know, courtesy of Ernest Rutherford, that it is the number of protons that dictates the identity of an element, not necessarily its atomic mass, as Mendeleev had thought.

- The second order of organization is in the columns of the table. Mendeleev had chosen his columns in such a way that each contained compounds with similar types of properties. For example, lithium, sodium, and potassium all react similarly to one another, so they reside in the first column.

- But what Mendeleev didn't know—what he couldn't have known in his day—was that the reason that these elements reacted so similarly is that they share a similar valence shell electron configuration. We have the benefit of understanding that it is the electron configuration of each element that gives it its own unique reactivity and that similar valence shell configurations lead to similar chemistries.

- By arranging columns of similar elements, we automatically create rows within the table. More importantly, each row begins with the expansion of an element's electron cloud into a whole new principal energy level.

- This level of organization is remarkable. The most remarkable thing about the table is how such a simple and elegant method of categorizing elements can explain the most complex properties of the most exotic known elements.

- When we organize elements in this way—by increasing atomic number, with new rows beginning with the first electron to populate a new principal level—the resulting table is encoded with many trends in the properties of the elements, some of which are very intuitive and some of which you might find surprising, but all of which help us better understand the behavior of matter.

ATOMIC RADIUS

- Atoms are very small. Their radii are generally on the order of angstroms, or 10^{-10} meters in scale. If we make the simplification that all atoms are approximately spherical, then we can report on their size by cataloging the radius of each. When we do this, we find that most atoms are remarkably similar in size.

- Consider the smallest and largest known atoms by radius: hydrogen and cesium. Interestingly, they are both group 1 atoms. Despite having an atomic mass about 133 times greater than a hydrogen atom, a cesium atom has a radius that is only about 10 times bigger.

- This is because as we look at increasingly massive atoms within a group, we are indeed adding more and more energy levels to the electron cloud, making it larger, but we are also adding protons. The electrostatic attraction between these increasingly positive nuclei of larger atoms and negatively charged electrons partially counterbalances the growth.

- You might think that, being so small in the first place, minute differences in the size of one atom versus another are unimportant. But very small changes in the sizes of atoms can have a profound effect on the properties of the materials they comprise.

- Each of the elements in group 8—helium, neon, argon, and krypton—has an electron cloud with a progressively larger and larger set of shells. This is what drives the trend in size. Valence shells are very large, and progressively adding more and more of them results in creating an atom that is larger and larger. So, the trend is that the radius of an atom decreases as we move up a column; in other words, it increases as we move down a column.

- Consider what happens as we move across a row of the periodic table—for example, the second row: lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, and neon. In this case, we can't use valence shells to try to determine which is larger because they all have the same valence shell. This is no longer the driving force in the radius of these atoms.

- Instead, what drives their size is the positive charge on their nucleus. As we go from left to right across a table, elements become more massive, but most of that mass is concentrated in their nucleus. When we add extra protons, we get extra charge.

- On the left of the row, lithium has a nucleus containing only 3 protons, and on the right of the row, neon contains 10 protons. This means that the nucleus of neon pulls much harder on those electrons in the second shell and therefore results in a squeezing down of the valence shell.

- The counterintuitive idea that a more massive element could actually have a smaller radius is easily justified when we consider the effects of this nuclear charge. This trend—decreasing atomic radius as we go left to right across a row—is driven by the charge on the elements and nucleus.

- Both of these trends hold well for *s*- and *p*-block elements, and it even works as a general trend for *d*- and *f*-block elements, but the complexity of the *d* and *f* subshells can sometimes cause slight deviations from this trend.

IONIC RADIUS

- Just as important as understanding trends in atomic size is the understanding of trends in the size of ions. Just as with atomic size, let's focus on the *s*- and *p*-block elements, because they are the most well behaved.

- As an example, let's consider one column of the periodic table, group 1. Group 1 atoms tend to form +1 ions to achieve an octet of electrons. The size of each positively charged ion increases dramatically as we step down the periodic table. The reason is that as we work our way down a column, we are adding additional energy levels to the ion's electron cloud.

- Trends in ion sizes across rows are a bit less regular, because the quest for octets makes it more attractive for elements like those in groups 1 through 4 to lose electrons to form common ions. This means that they lose a valence shell on ionization, making them much smaller, while those in groups 5 through 7 prefer to gain electrons to form an octet, retaining and expanding their valence shell.

IONIZATION POTENTIAL

- Some elements are easy to find as neutral atoms in nature. Elements like inert argon gas in our atmosphere or metallic gold in the ground are rare, but when one of these elements is found, it is almost always as neutral atoms.

- But not all elements are so well behaved. Potassium, for example, is never found as isolated neutral potassium atoms. Rather, it seems to always appear as a positively charged cation with a charge of +1.

- Why do some elements seem to enjoy simply being themselves, while others tend to appear as ions of specific charges when we find them?

- Neutral atoms can be excited from their so-called ground states using light or electricity. When the proper amount of energy is added, electrons can be promoted into higher energy levels within the atom, creating an excited state in which the atom still owns that electron, but it occupies an orbital farther out than usual.

- Different atoms require different amounts of energy to promote electrons—a property that gives each one a unique line emission spectrum, allowing us to make a beautiful rainbow of colors using just a few different elements in combination with one another in neon lamps.

- Imagine what would happen if we imparted a neutral atom with so much energy that its outermost electron wasn't promoted to a higher energy level, but instead was ejected from the atom, essentially promoting it to the infinity level, if such a thing exists. When this happens, the loss of a negatively charged electron means that a cation is formed—a positively charged version of the atom that has drastically different properties than the atom itself.

- The amount of energy needed to remove an electron from an atom and create a cation with a +1 charge is known as its first ionization energy. The ionization energy of elements trends periodically: First ionization energy increases as we move up and to the right on the periodic table.

ELECTRONEGATIVITY

- The flip side of the first ionization potential coin is what is known as electronegativity. Just as first ionization potential measures how easily an electron is lost by a neutral atom, electronegativity refers to how easily an electron is picked up by a neutral atom.

- The trend is reversed from that of first ionization potential, with elements like fluorine having the greatest electronegativity while elements like cesium and francium have very small electronegativities.

- We report electronegativities of atoms in special units on a scale named for American chemist Linus Pauling. The Pauling scale ranges from 0 to 4, with 4 being the most electronegative element that is known: fluorine.

- At the far left and bottom of the table are cesium and francium, both of which have the lowest electronegativity of any known element at 0.8.

- The reasons for this trend are similar to those for ionization potential trends. Atoms want to acquire electrons to form octets, so elements like fluorine, which are just a single electron shy of an octet, are extremely hungry for an electron.

- On the other hand, there are elements at the left of the table that are so far from an octet that they can't possibly benefit from acquiring an electron.

- The obvious exception to this trend is the noble gases, which already have a full octet. Because they are already happy, they have no strong tendency to gain or lose electrons.

- We see additional fascinating trends in the way elements ionize, particularly in the *s* and *p* blocks of the periodic table.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 261–290.
UC Davis ChemWiki, "Periodic Trends."
http://chemwiki.ucdavis.edu/Core/Inorganic_Chemistry/Descriptive_Chemistry/Periodic_Trends_of_Elemental_Properties/Periodic_Trends.

QUESTIONS

1. Element 55, cesium, is an alkali metal much like the lithium, potassium, and sodium metals used in the demonstration from this lecture. Considering the periodic trends of first ionization potential, suggest why cesium was not used in the demonstration.

2. Fluorine gas is highly reactive and toxic, but we use the element fluorine to treat our drinking water as a fluoride ion. What is the difference between elemental fluorine and fluoride ion, and how does the periodic trend in electronegativity predict that fluoride ion will be much less reactive than pure fluorine gas?

3. Rank the following elements in order of increasing electronegativity: fluorine, carbon, oxygen, cesium, and lithium.

Answer
3) Ce, Li, C, O, F.

Compounds and Chemical Formulas

LECTURE 8

If fewer than 100 naturally occurring elements exist, and only a few dozen more have been created by man, then how do we live in a world with countless millions of different materials? In this lecture, you will learn about molecules, which are any discrete group of atoms linked by chemical bonds. You will also learn about compounds, which are molecules in which at least 2 different elements are present. Finally, you will discover 2 common methods chemists use to convey the composition of molecules and compounds: the empirical formula and the molecular formula.

MOLECULES

› In the first decade of the 1800s, John Dalton proposed the law of multiple proportions based on his observation that elements only combine in simple whole-number ratios to create new materials. The logical interpretation of this is that groups of atoms combine to form discrete entities in which those atoms are somehow attached to one another.

› When atoms of all of the elements begin to combine with one another in this way, the possibilities are practically infinite. These conjoined groups of atoms are called molecules.

› Elements can exist as isolated atoms in certain cases. For example, the elements helium and neon tend to exist only as isolated atoms—also called monoatomic. Not all elements do this. Some elements exist in discrete, small bonded clusters of atoms.

- We don't find oxygen and nitrogen in these kinds of states in nature. Instead, we tend to find them chemically linked to other atoms of the same kind. Specifically, nitrogen and oxygen tend to appear as diatomic molecules, meaning that 2 atoms are linked together through a chemical bond.

- When this happens, we put a subscript next to the elemental symbol—in this case, a subscripted 2, indicating that we're talking about a molecule consisting of 2 atoms of the same kind linked together. Nitrogen is written as N_2; oxygen is written as O_2. There are other elements that exist as even larger molecules, such as phosphorus (P_4) and sulfur (S_8).

- Dividing a sample of molecular oxygen into parts will give you smaller and smaller samples of that molecular oxygen. But once you reach a single O_2 molecule, dividing it would yield oxygen atoms, which have quite different properties. This is just one reason why understanding the concept of molecules is so crucial to the study of chemistry.

COMPOUNDS

- Atoms of the same element can be attached to one another to form molecules of that element that have properties that are different than the isolated atoms. But the existence of those few molecules still fails to explain the tremendous diversity that we observe in the matter around us.

- To explain that, we have to consider that all atoms within a molecule need not be of the same element. When we account for this, suddenly a massive collection of potential combinations springs to life, each with its own unique set of properties and reactivity.

- Consider oxygen, hydrogen, and carbon—2 gases and a dark solid. Using just these 3 elements, scientists and mother nature can create compounds as diverse as vinegar, sugars, poisonous substances, and healthy compounds.

- Combining the same elements in different ways can mean the difference between a carcinogen and a medicine, so clearly it isn't just enough to say that a compound is made of carbon, oxygen, and hydrogen. We need to communicate the atomic composition of molecules in a concise and simple way if we are going to have a meaningful discussion of chemistry. Chemists accomplish this using the same system for compounds that they do for molecules of pure elements.

- Early attempts to determine the composition of a compound could only divulge the ratio of its constituent elements. This type of formula is called an empirical formula.

- In the days of pioneers like Lavoisier and Faraday, the composition of materials could only be determined by simple techniques like combustion analysis, in which a compound is burned in excess oxygen and the mass of the by-products is determined. From these masses, the simplest whole-number ratio of elements could be determined by a quick calculation.

- Benzene is a hydrocarbon, meaning that it is a compound consisting only of carbon and hydrogen atoms bonded together. But how much of each element does it contain? One way of determining this is to use oxygen gas to combust benzene, and then measure the amount of carbon dioxide and water that is formed in the process.

$C_?H_?$	O_2	→	CO_2	H_2O
benzene	oxygen		carbon dioxide	water
x g (grams)	(excess)		5.72 g	1.17 g

- If we run this experiment, we determine that after combustion, we have 5.72 grams of carbon dioxide (CO_2) and 1.17 grams of water (H_2O). The 1.17 grams of water tells us that at 18 grams per mole, and 2 moles of hydrogen atoms for every 1 mole of water molecules, we have a total of 0.13 moles of hydrogen in the system.

- The amount of carbon dioxide created tells us that at a molecular weight of 44 grams per mole, and 1 mole of carbon atoms for every mole of carbon dioxide, our sample must have contained 0.13 moles of carbon.

$$\left(\frac{1 \text{ mol } CO_2}{44.0 \text{ g } CO_2}\right)\left(\frac{1 \text{ mol C}}{1 \text{ mol } CO_2}\right) = 0.13 \text{ mol C}$$

$$\left(\frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O}\right)\left(\frac{2 \text{ mol H}}{1 \text{ mol } H_2O}\right) = 0.13 \text{ mol H}$$

- Now we have all the information we need to construct the empirical formula, which, most simply stated, is $C_{0.13}$ $H_{0.13}$. But the ratio 0.13:0.13 is the same as the ratio 1:1, making the formula C_1H_1. We can emit the 1s, too, because they're understood. Therefore, the empirical formula of a benzene molecule is simply CH.

- Using techniques available to scientists around 1800, we can determine that benzene is a compound with equal numbers of hydrogen and carbon atoms. But just how big are these molecules? Does a single benzene molecule contain just one atom of each? Does it contain 2 of each? What about 3 of each, and so on? All of these possibilities are consistent with the empirical formula we determined.

- To be absolutely sure about the makeup of individual molecules of a compound rather than its bulk makeup, scientists of this time would need more information. The empirical formula simply wasn't enough.

- This leads to the second method of communicating the makeup of a compound: the molecular formula. In this system, just as with empirical formulas, we use the elemental symbols, each with a subscript: C_6H_6.

- The difference is that this time, the subscript indicates exactly how many of those atoms are present in a single molecule of the compound—not their simplest ratio, but their exact quantity. This is a more useful representation of a molecule's composition, because it relieves some of the ambiguity about its makeup.

- The key to determining the exact molecular formula of a compound is to know not only its empirical formula, but also another crucial parameter that eluded Lavoisier and Dalton: molecular mass.

- Although Dalton was able to get the ball rolling on determining relative atomic masses and empirical formulas in the first decade of the 19th century based on his law of multiple proportions, his techniques still did not allow him to do the same for molecules. So, we need to know how much a molecule weighs. But how do you weigh something as small as a molecule?

- The first successful determination of the weight of a molecule was reported by French chemist Jean-Baptiste Dumas in 1826. Dumas's technique did not require that a single molecule of a sample be isolated and weighed; instead, it relied on a keen observation regarding the densities of vapors. Dumas's technique relied on a very important observation made decades earlier by Avogadro.

- Solids and liquids contain molecules in close contact with one another. If we were to reduce the size of the molecules in a sample of solid or liquid, then that sample's volume should decrease accordingly. So, a given volume of solids or liquids will contain differing numbers of molecules depending on the size of those molecules.

- But Avogadro noted that in gaseous samples, molecules are not in constant contact with one another. They are so far apart that their size makes up a negligible fraction of the space that they occupy. So, reducing the size of the molecules in a gaseous sample does not have an effect on the volume the sample occupies.

- It turns out that this is exactly the case. And the exact volume occupied by 1 mole of gas molecules at 1 atmosphere of pressure at 0° centigrade is 22.4 liters.

- So, under standard conditions, 22.4 liters of gas contains exactly 1 mole of particles, no matter what the sample is made of. By measuring the density of pure gases under similar conditions, Dumas was able to begin cataloging their relative masses.

- For example, Dumas could have measured the mass of 22.4 liters of benzene vapor, determining that it contained 72.11 grams of benzene. Based on his understanding that 22.4 liters of gas on his lab bench must contain exactly 1 mole of gas, he could easily calculate a molar mass of 78.11 grams per mole of benzene.

$$\left(\frac{78.11\text{ g benzene}}{22.4\text{ L benzene}}\right)\left(\frac{22.4\text{ L benzene}}{1\text{ mol benzene}}\right) = 78.11\text{ g/mol benzene}$$

- Combining this new piece of information, the molecular mass, with the empirical formula determined previously can lead to the molecular formula of a compound.

- The following are a few of the potential molecular formula based on our previously determined empirical formula. All of them have the same simplest whole-number ratio, one carbon to one hydrogen, but which is actually the molecular formula for benzene?

$$\begin{array}{|c|ccccccccc}
\mathrm{CH} & 1 & \times & (12.01\text{ g/mol}) & + & 1 & \times & (1.01\text{ g/mol}) & = & 13.02\text{ g/mol} \\
\mathrm{C_2H_2} & 2 & \times & (12.01\text{ g/mol}) & + & 2 & \times & (1.01\text{ g/mol}) & = & 26.04\text{ g/mol} \\
\mathrm{C_3H_3} & 3 & \times & (12.01\text{ g/mol}) & + & 3 & \times & (1.01\text{ g/mol}) & = & 39.06\text{ g/mol} \\
\mathrm{C_4H_4} & 4 & \times & (12.01\text{ g/mol}) & + & 4 & \times & (1.01\text{ g/mol}) & = & 52.08\text{ g/mol} \\
\mathrm{C_5H_5} & 5 & \times & (12.01\text{ g/mol}) & + & 5 & \times & (1.01\text{ g/mol}) & = & 65.10\text{ g/mol} \\
\mathrm{C_6H_6} & 6 & \times & (12.01\text{ g/mol}) & + & 6 & \times & (1.01\text{ g/mol}) & = & 78.12\text{ g/mol}
\end{array}$$

- To determine this, we have to calculate what the molecular weight, or molar mass, should be for compounds with these formulas and find the one that matches our observed data.

- For example, if the molecule were simply one carbon and one hydrogen bonded together, we would expect it to have a molar mass of 13.02 grams per mole, because carbon has a molar mass of about 12 and hydrogen has a molar mass of about 1.

- C_6H_6 gives us a molar mass that is practically identical to what we measured experimentally. This tells us that the structure of benzene must actually be a molecule consisting of 6 carbons and 6 hydrogens.

- We've graduated from knowing just the ratio of atoms in a molecule of benzene to knowing exactly how many of each type of atom are in a molecule of benzene. When the structure of benzene was finally solved, it was confirmed that benzene is, in fact, C_6H_6.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 52–55.
UC Davis ChemWiki, "Chemical Formulas."
http://chemwiki.ucdavis.edu/Wikitexts/University_of_Waterloo/Chem120/Stoichiometry/Chemical_Formulas.

QUESTIONS

1. Both benzene (C_6H_6), a somewhat stable liquid and industrial solvent, and acetylene (C_2H_2), a very reactive gas commonly used in welding applications, have the empirical formula CH. How is it possible for such different compounds to have the exact same empirical formula?

2. The simple sugar glucose has an empirical formula of CH_2O and a molar mass of 180.16 grams per mole. What is the molecular formula of glucose?

Answer
2) $C_6H_{12}O_6$.

Joining Atoms: The Chemical Bond

LECTURE 9

We know that molecules exist and that they are critical to explaining nature's incredible variety of materials. But what binds atoms together into molecules and compounds, and how and why do they do this? The answer to this question is a phenomenon known as chemical bonding—the subject of this lecture. Specifically, in this lecture, you will learn about the 3 classes of chemical bonding: ionic, covalent, and polar covalent bonds.

CHEMICAL BONDING

- In the first decade of the 1800s, John Dalton wondered how various combinations of elements can create substances with such diverse properties. The obvious answer is that multiple atoms combine to form more complex structures with properties fundamentally different than those of the atoms comprising them.

- Dalton did not have the benefit of understanding the structure of the atom, so he imagined that atoms somehow physically hooked themselves together to create small clusters of atoms that comprise compounds. He felt that this explanation would account for his earlier observation of the law of multiple proportions, which states that atoms combine in whole-number ratios to form compounds.

- Simply defined, chemical bonding is an energetically beneficial interaction between atoms that confines them to a fixed distance from one another in space.

- The distance between 2 bonded atoms is commonly just an angstrom or 2—not much larger than the radius of an atom itself—so we are talking about very close associations of atoms. When atoms get this close to one another, their electron clouds—being made from negatively charged electrons—repel one another. So, atoms can only ever get so close to one another before they start pushing against one another due to electrostatic repulsion.

- But why would atoms ever want to get close to one another? If all atoms' electron clouds push against one another, why not just keep their distance? What is the driving force that brings atoms together?

- The energetic driving force that brings atoms together is the fact that all atoms strive to form valence octets. This powerful desire of atoms to have a full valence shell makes them willing to get close to one another when a mutually beneficial arrangement can be reached. When this is the case, atoms will stay within a specific distance from one another—a distance at which the attractive forces they experience are balanced by their mutual repulsion. This is the fundamental description of a chemical bond.

- Chemical bonds are actually a continuum, but are generally viewed as falling into one of 3 basic classes: ionic bonds and covalent bonds make up the extremes, and polar covalent bonds fill in the gray areas between them.

IONIC BONDS

- Ionic bonds are the kinds of bonds that are known to hold together many familiar substances, including table salt, or sodium chloride. In the case of ionic bonds, electrostatic attraction holds atoms together at a fixed distance.

- Electrostatic attraction results when atoms are ionized. And the driving force behind ionization is the octet rule. When we pair 2 atoms that have a tendency to form ions of opposite charges, there is a mutually beneficial exchange of electrons that can take place between them.

- Let's consider 2 elements, sodium and chlorine, which combine to form table salt, the compound called sodium chloride. We know from trends in electronegativity and the periodic table that chlorine atoms are fairly electromagnetic, with an electronegativity of about 3.0. Sodium, on the other hand, is not very electronegative, with an electronegativity of about 0.9.

- This means that chlorine is very eager to accept an electron. Sodium doesn't really care about accepting electrons; in fact, it really likes to let go of them. The ionization energy is quite low for alkaline metals.

- When a sodium atom and a chlorine atom get close to one another, an exchange happens that's mutually beneficially. Sodium likes to lose electrons, and chlorine likes to gain electrons. The outermost electron in the $3s^1$ shell of sodium can simply hop over to the chlorine and fill chlorine's third valence shell and octet. When this happens, the electron configuration of the new ions are neon and argon.

- The sodium has the electron configuration of a noble gas. The chlorine also has the electron configuration of a noble gas. This drives the bonding behavior of the 2 atoms. It's the electrostatic attraction between them that causes this bond to form.

- So, when a sodium and a chlorine atom are in very close proximity to one another, they can exchange one electron and create a very powerful attraction between the 2 resulting ions.

- But ionic bonds are not necessarily isolated connections between 2 atoms. When a mixture of ions like sodium and chloride get together, they can create a huge, repeating structure known as a crystal lattice. This network of ionic bonds can stretch for billions upon billions of atoms and is so strong that to overcome it and melt sodium chloride requires temperatures above 1000° Kelvin.

COVALENT BONDS

- The other type of bond that we commonly encounter in chemistry is the covalent bond, which forms as the result of electron sharing between 2 elements—not as the result of electron transfer, as in ionic compounds.

- We know that atoms are always trying to find ways to fill their valence shells. Gaining or losing electrons gives many elements a mechanism by which they can obtain an octet, but that comes with some problems. The first is the buildup of charge as electrons are gained or lost with no change to the number of protons in an atom's nucleus.

- Ionization potentials increase dramatically as each subsequent electron is removed from an atom. At some point, this simply isn't going to be a feasible way to get an octet.

- Then, there is the consideration of exactly where the lost electrons go. In the case of ionic bonding, this problem is solved by a different element receiving the electron and forming an anion. This is a great arrangement in cases like sodium chloride and magnesium oxide, because each of these compounds combines one very electropositive element with one very electronegative element. This makes electron exchange a snap.

- But what if 2 atoms have much more similar electronegativities? Take the extreme example of a hydrogen molecule, which contains 2 of the exact same type of atom. Which is going to give up its electron, and which will receive one? The answer is neither. They would rather be neutral atoms than take on opposing charges. The ionic bonding arrangement simply isn't energetically beneficial enough to happen.

- But there is a second option: covalent bonding. Instead of an exchange of electrons, these 2 atoms can simply share their electrons, fooling one another into thinking that each has a full first energy level. At a specific distance, the atoms are close enough that their valence shells overlap, but far enough apart that they do not repel one another electrostatically.

POLAR COVALENT BONDS

- Ionic and covalent bonds are the 2 more extreme forms of chemical bonds. Ionic bonds form when 2 elements of drastically different electronegativities, such as a metal and a nonmetal, get together. In this case, one element completely relinquishes one or more valence electrons to another, forming an ionic bond.

- At the other end of the spectrum are bonds between nonmetal atoms of the exact same type, and therefore the exact same electronegativity. These atoms can share pairs of valence electrons with one another to form covalent bonds.

- But there is a third situation—a gray area—in which we are dealing with 2 different elements whose electronegativities are not quite the same. Take the example of hydrogen and chlorine.

- Chlorine has an electronegativity of about 3.0, and hydrogen has an electronegativity of about 2.1. This is not drastic enough for a complete exchange of electrons, so we expect a covalent bond to form when these 2 atoms join together. But although chlorine doesn't pull strongly enough on hydrogen's shared electron to completely liberate it from the hydrogen atom, it does pull harder than its counterpart.

- The result of this is an uneven sharing of electrons, in which the shared pair spends a bit more of its time more closely associated with the chlorine. This creates a slight charge imbalance between the 2 bonded nuclei—not enough to call them true ions, but enough that they are no longer neutral.

- We call this type of bond a polar covalent bond. They are called polar bonds because of the charge separation. It creates a negative end and a positive end of the bond. This is not a full unit of charge, as in an ionic bond, but it is a real, permanent charge nonetheless.

- We use a Greek lowercase delta (δ) to indicate that these are so-called partial charges on the atoms. In this case, some negative charge builds up on the oxygen and some positive charge builds up on the hydrogen.

THE STRUCTURE OF COVALENT BONDS

- The sharing of electrons can lead to covalent or polar covalent bonds. The Rutherford model of the atom can be used to demonstrate how bringing certain atoms into proximity with one another can lead to an energetically beneficial sharing of electrons, but the Rutherford model is an oversimplification. To really understand the structure of bonded atoms, we have to use what we know about the electronic structure of the atom.

- To create a covalent bond, electrons are shared between 2 atomic orbitals, one from each atom. But not all atomic orbitals are created equal, so the bonds that they can form are not always equal, either.

- In general, there are 2 classes of covalent bonds that can form: sigma bonds and pi bonds. Sigma bonds are the result of orbital overlap directly between the 2 bonded nuclei on the internuclear axis. These kinds of bonds can form when either an *s* orbital or *p* orbital overlap. Having the shared electrons directly between the 2 bonded atoms leads to a stable bond, so sigma bonds tend to form first.

- But this creates a problem when trying to understand multiple bonds, such as the double bond holding oxygen together or the triple bond holding a nitrogen molecule together.

- The problem is one of geometry. Only one set of orbitals can overlap directly between the 2 atoms. But there are other ways to achieve additional overlap. The side-on overlap of 2 sets of *p* orbitals can create a shared space that holds 2 more sets of bonding electrons.

- These kinds of bonds are called pi bonds. In this case, the bonding electrons are not directly in between the bonded atoms. So, pi bonds, though stable, aren't as stable as sigma bonds.

- All of this means that when 2 atoms get together to form a covalent bond, the first bond between them is always sigma, and any additional bonds are always pi.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 55–67, 1004–1006.

UC Davis ChemWiki, “Covalent Bonding.”
http://chemwiki.ucdavis.edu/Core/Theoretical_Chemistry/Chemical_Bonding/Covalent_Bonding.

QUESTIONS

1. For chemical reactions to take place, bonds must not only form but often break. If the formation of chemical bonds releases energy and increases stability, why would chemical bonds ever break?

2. How does our model of metallic bonding help predict that cesium is one of the softest and easily melted elements known to humankind?

3. Which type of bond (covalent, polar covalent, ionic, or metallic) do you most expect to form between each of the following pairs of elements?

    a. Potassium and oxygen

    b. Silicon and oxygen

    c. 2 oxygen atoms

    d. 2 cesium atoms

Answers

3a) ionic; 3b) polar covalent; 3c) covalent; 3d) metallic.

Mapping Molecules: Lewis Structures

LECTURE 10

The scientific community's understanding of chemical bonding began to blossom in the early part of the 20th century, but without the ability to actually see molecules and atoms, the path to understanding what holds them together has been a long and arduous one. In this lecture, you will be introduced to one of the oldest and still most widely used techniques that chemists use to draw molecules—a drawing style called the Lewis structure.

COVALENT COMPOUNDS

- At the turn of the 19th century, American chemist Gilbert N. Lewis was hard at work in Berkeley, California, trying to understand the relationships between valence electron interactions and bonding.

- Lewis knew from earlier research that smaller elements have a powerful tendency to seek out valence octets. So powerful is this desire that some atoms are willing to lend their electrons to others in the process of covalent bonding.

- Lewis had already begun sketching atoms in his lectures at Berkley using dots at the corners of a cube to depict their valence electrons—a convenient way to demonstrate the octet rule, because cubes have 8 corners.

- As Lewis continued to refine his tool for understanding valence electrons, he began placing the electrons not at 8 corners, but around the atom on 4 sides in pairs instead. He found this notation style useful in his teaching and expanded his use of dots to create a shorthand system to track the location of valence electrons in not only atoms, but also in molecules.

- If we look at the Bohr model for each of the elements in the second row of the periodic table—lithium through neon—it's very simple to determine what the Lewis structure should be because the Bohr model so clearly shows what the valence electron count is, and that's what Lewis was interested in.

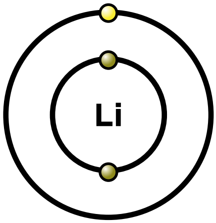
- The Bohr model of a lithium atom is shown at right. It's a $1s^2$ $2s^1$, and the $2s^1$ lives out in the valence shell, so because Lewis structures are only concerned with valence shell electrons, we only put one dot on the lithium atom to indicate a neutral lithium atom with a $2s^1$ electron.

- For the next element, beryllium, we add a new valence electron for a total of 2, and therefore we use 2 electrons in the Lewis structure. For boron, which has 3 valence electrons, we place the 3 electrons around the boron. The trend continues as we move across the row, with carbon having 4, nitrogen having 5, oxygen having 6, and so on, until we reach neon—at which point we wrap around and begin anew with only one dot on the Lewis structure for sodium.

- Any time 2 atoms come together to create a covalent bond, they share 2 or more electrons with one another. In a Lewis structure, this sharing of electrons is demonstrated by placing the corresponding dots between the 2 atoms.

Lithium

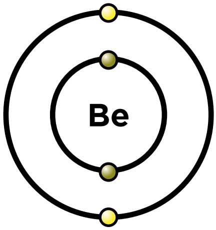
BOHR MODEL



LEWIS STRUCTURE

Beryllium

BOHR MODEL



LEWIS STRUCTURE

- The simplest example of this is the Lewis structure for diatomic hydrogen gas, in which the electron for each hydrogen is placed between the 2 symbols. When this happens, a single bond consisting of 2 electrons joins the atoms, and this arrangement fools each hydrogen atom into believing that it has 2 valence electrons all its own.

- This helps to explain why we find hydrogen as a diatomic molecule in nature, rather than as isolated atoms of hydrogen.

H_2

Helium

- If we apply Lewis's technique to hydrogen's neighbor on the periodic table, helium, we see something very different. The dot structure for isolated helium atoms already shows 2 electrons in its valence shell. This means that helium atoms do not need to bond to one another to fool themselves into thinking that they have a $1s^2$ configuration—they actually do have a $1s^2$ configuration.

- So, in this case, it becomes clear that helium should exist normally as isolated atoms, instead of diatomic molecules. This is in fact the case.

- Lewis structures also make it very simple to determine the bonding in relatively simple molecules, such as neon, fluorine, oxygen, and nitrogen.

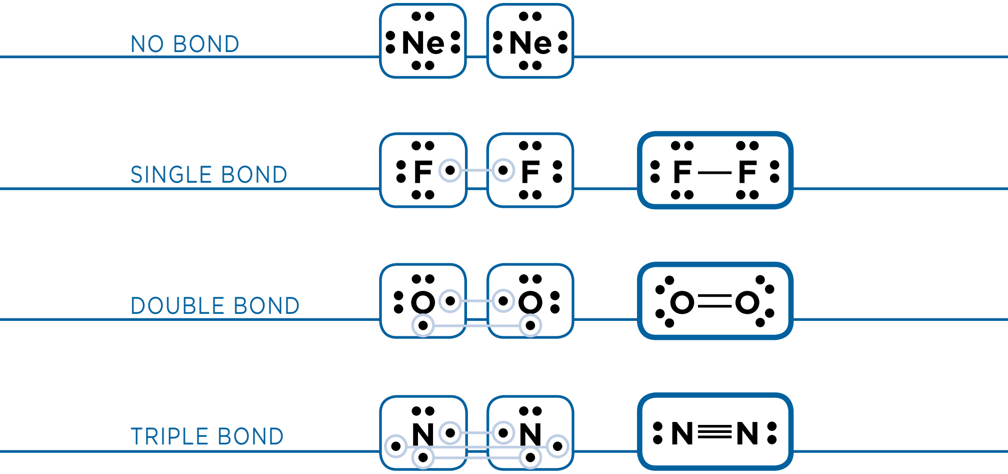
- Will 2 neon atoms bond? Each neon already has its own octet. We don't anticipate any bond to form in this case because there is no driving force.

- Fluorine, on the other hand, will form a bond, and that's because fluorine atoms have to get together to share electrons. Because of the sharing of the central electrons in the Lewis structure, each fluorine believes that it has 8 valence electrons.

- Oxygen is going to bond to try to form an octet. The Lewis structures show that when 2 oxygen atoms combine, they form a double bond, resulting in each oxygen atom having 8 valence electrons.

- The trend continues. When 2 nitrogen atoms get together, they form a triple bond, in which each nitrogen atom believes that it has an octet. When we experimentally verify the bonding behavior of these elements, this is exactly the trend that we see.

- With Lewis structures, when bonds form, we often replace the symbol for the bonding pair of electrons—2 dots—with a single bar.



- Lewis structures of these simple molecules allow us to explain certain observations, such as the solid stability of nitrogen gas; the relatively high reactivity of halogens like fluorine gas, and the tendency of noble gases like helium to exist as isolated atoms.

FORMAL CHARGE

- But Lewis's invention gives us even more information about the structure and properties of molecules. With all of the electron sharing that goes on in molecules, you can probably imagine that separation of charge is a very real possibility. If all of that electron sharing results in an unusually high electron density around an atom, it might start to feel some negative charge, and conversely an unusually low electron density would make it feel more positive.

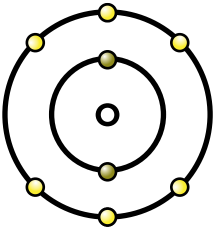
- This kind of charge buildup is called formal charge. In general, atoms prefer not to carry charge, so if we have a way to scan molecular structures for this kind of destabilizing phenomenon, we can begin to explain why certain compounds are more stable than others, or even how and why certain compounds react. And the perfect tool to do this is the Lewis structure.

- Oxygen's electron configuration can be easily divined from the periodic table: $1s^2\ 2s^2\ 2p^4$. Its Bohr model and Lewis structure lead us to the conclusion that oxygen should have 6 valence electrons if it's going to be a neutral oxygen atom. But when atoms bond together, they share electrons, so there's a potential for that sharing of electrons to throw off this balance of charge.

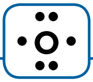
- When an oxygen molecule forms, does each oxygen experience a greater negative charge density than it ordinarily would as a lone atom? If so, we have to compensate for that.

Oxygen

BOHR MODEL



LEWIS STRUCTURE



Neutral oxygen atoms have 6 valence electrons.

- When it comes to the octet rule in bonding, we count bonded pairs as 2 electrons for each atom, but bonded electrons spend a little time on one a little time on the other, and their charge effect is distributed, so a bonding pair of electrons would only count as one negative charge for any given atom that's involved in that bond.

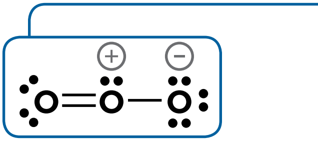
- That means that oxygen in O_2 needs 6 electrons around it to have its charged balanced from its nucleus, and if we look at the Lewis structure, we see that we have 2 lone pairs, so that counts as 4 total electrons and 2 bonded pairs.

- But those 2 bonded pairs spend a portion of their time in proximity to another oxygen, so their overall effect on the charge is only half of that. That means that each of the oxygen atoms—as far as charge concerned—believes that it has 6 electrons. That means that their formal charges are 0. They are both happy.

- Ozone, or O_3, is another form of molecular oxygen. An O_3 molecule would have a Lewis structure like what's shown here. The oxygen on the left side of the molecule should have 6 electrons nearby if it's going to have a formal charge of 0, and indeed there are 2 nonbonding pairs and 2 bonding pairs for a total charge effect of 6. This is another happy oxygen, but things change when we get to the next part of the molecule.

- In the case of the central oxygen of O_3, there are 2 bonding pairs and one lone pair for a total of 5 electrons, as far as charge is concerned, so the central oxygen has a formal charge of +1, which makes it less stable. Naturally, elements like to be neutral when they can.

O_3



- The oxygen on the right has 3 lone pairs and a bonding pair for a total charge effect of 7. This means that this oxygen believes that it has too many electrons. It has a formal charge of −1. We write these formal charges onto the molecules using a circle charge sign: +1 for the central oxygen and −1 for the structure.

- Ozone simply isn't as stable as diatomic oxygen, and we can account for that because of the formal charge differences that the Lewis structures predict. Our use of Lewis structures gives us a way to illustrate why diatomic oxygen, or O_2, is ever-present near the surface of the Earth, while ozone, or O_3, tends to form only in extreme conditions, such as those found in the Earth's outer atmosphere, which is bathed in solar radiation, or in bolts of lightning, releasing extreme amounts of energy.

LEWIS STRUCTURES OF COMPOUNDS

- Chemistry is about diversity: the study of not just the 100 or so elements, but the virtually infinite library of compounds that can form when those elements are combined. And Lewis structures give us a wonderful way to illustrate the connectivity of atoms in compounds, demonstrating the octet rule and allowing us to predict formal charges in all kinds of compounds.

- There is a series of steps that we need to follow to construct a proper Lewis structure.
  - Take all of the atoms present in the compound and count the electrons in their valence shells.
  - Place the least electronegative element in the center of the molecule.
  - Create a sigma bond network.
  - Fill the octets of the outer atoms with the remaining pairs.

- If we have just enough electrons to get the job done, we can stop. If we don't have enough electrons, we can resort to making pi bonds. If we have too many electrons for this process, we're allowed to expand the octet of the central atom, as long as it's in the third row or beyond.

- CCl_4, commonly called carbon tetrachloride, is formally used as a dry cleaning solvent and commonly used in the chemistry lab. It contains one carbon and 4 chlorines. We can tell that from its molecular formula.

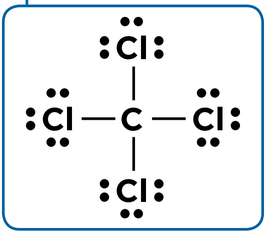
- To determine the Lewis structure of CCl_4, the first step is to count the valence electrons for all of the atoms. From the periodic table, we can determine that carbon should have 4 valence electrons, and each chlorine should have 7, so the total budget for this procedure is 32 electrons.

- The next step is to place the least electronegative element—in this case, carbon—in the center of the molecule and create a bonding network that holds all of the other atoms to that central molecule. Creating the 4 bonds that hold each of these chlorine atoms in place consumes 8 electrons from the valence electron budget, leaving 24 electrons to satisfy the octet rule for everyone in this molecule.

- Next, we take all of the chlorines and fill their valence shells completely. When we do this, we have 6 additional electrons per chlorine. For chlorine's total, that means we've used 24 more electrons. We've exhausted our budget, but we're done because all of the chlorine atoms believe that they have an octet from a bonding perspective. The central carbon believes that it has an octet, too.

- All of the atoms in this compound are satisfied. The following is a Lewis structure for carbon tetrachloride.

CCl_4



READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 310–311, 317–328.
Cobb and Goldwhite, *Creations of Fire*, pp. 310–313.

QUESTIONS

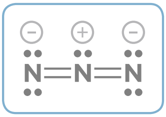
1 Why is it that the least electronegative element most often finds itself as the central atom in the types of small molecules that were investigated in this lecture?

2 Why is it that expanded octets only occur on central atoms in the Lewis structures that were discussed in this lecture?

3 Azide ions (N_3^-) are reactive ions whose decomposition is sometimes used to inflate automobile airbags. Draw a Lewis structure for azide ion and use formal charges to explain why it is so unstable.

Answer

3)



All atoms in azide ion have formal charge associated with them, helping explain why this ion is so reactive.

VSEPR Theory and Molecular Geometry

LECTURE 11

The molecular formulas of molecules give us a recipe for how many of each atom must be present and how they are connected, but they fall short of giving us another critical piece of information: how those connected atoms are arranged in space. And when it comes to determining how molecules will behave, the geometric arrangement of their atoms can be every bit as important as their identity and connectivity. In this lecture, you will learn about molecular geometries.

MOLECULAR GEOMETRIES

- A molecule of O_2, or diatomic oxygen, is the allotrope of oxygen that we encounter most commonly at the Earth's surface. It consists of 2 oxygen atoms connected by a double bond. With a defined average bond length and only 2 points (those defined by the oxygen atoms), there is only one geometry that can define this molecule: a straight line.

- Chemically inert nitrogen gas, toxic chlorine gas, and the powerful acid hydrochloric acid are all examples of simple diatomic molecules. If we try to move one atom relative to the other in molecules like these, the molecule simply rotates. We may change its orientation, but we aren't changing the geometric relationship between the 2 atoms making each up. We're simply making the molecule tumble.

- So, diatomic molecules can only take on one possible arrangement of atoms as a result of their simple makeup. If we try to move one of the atoms, we only really succeed in rotating the linear construct.

- But consider a molecule with 3 atoms, such as water, in which a central oxygen atom is bonded to 2 hydrogen atoms, for a total of 3 atoms per molecule.

- The addition of that third atom introduces a new wrinkle. If, just as before, we hold the molecule steady but move one of the atoms, something about this molecule changes. The 3 atoms define an angle, and that angle is altered when one atom moves relative to another.

- The Lewis structure of water is simple enough to construct, but when we try to translate that structure into a 3-dimensional molecule, we have to ask ourselves, are the 3 atoms all in a row? Or do they find themselves in a nonlinear orientation that defines an angle? If so, exactly what is that angle?

- All of these questions matter because their answers will come to bear on the physical and chemical properties of compounds containing more than 2 atoms. The answer to these questions lie in the ideas of a few great researchers who put their faith in Gilbert Lewis, using his 2-dimensional structures of atoms and simple molecules as a guide to create a theory that predicts the 3-dimensional structures of molecules.

- The theory is known as valence shell electron pair repulsion (VSEPR) theory. This relatively simple theory represents one of the scientific community's first attempts to connect what was known about atomic structures to molecular structures. It is remarkably effective when applied to simple molecules like water, and it is still often invoked in modern research.

- VSEPR theory hinges on a very important concept: the concept of electron domains. An electron domain is simply a concerted region of electron density in the valence shell of an atom.

- Where do we find regions of high electron density in the valence shell of an atom? That would be in the orbitals holding lone pairs and in orbitals forming bonds to other atoms. So, a lone pair would constitute an electron domain—and so would a single bond to another atom.

- Double and triple bonds also each collectively represent a single electron domain, because all of the electrons involved in the bond are in close proximity to one another. They share the same region of space, so they make up a single domain.

- To apply VSEPR theory to any small molecule, simply focus on the central atom of the molecule and ask a few questions about its electron domains and how they push against one another.
    1. What is the Lewis structure for the molecule? (We construct a Lewis structure, which helps us determine the central atom and the connectivity of the other atoms in the molecule.)
    2. How many electron domains are on the central atom?
    3. How can those electron domains best distance themselves from one another?
    4. What kind of geometry do the electron domains create around the central atom? (This is called the electron domain geometry.)
    5. When we ignore the presence—but not effects—of lone pair electrons, paying attention only to the atoms and the shape that they trace out, what geometry do we see among the atoms of the molecule?

GEOMETRIC POSSIBILITIES

- We could determine the geometry of every molecule known to man using VSEPR, but that would take a lot of time, so we need to take a new tactic. Fortunately, we have one. We can condense the analysis down to just a few generic possibilities by using generic markers for central atoms, connected atoms, and lone pairs of electrons.

- When we consider most small molecules, specifically those with just one central atom to which all other atoms or groups of atoms in a compound are connected, we can create a generic table of geometric possibilities using the following notation:

  - We will define the central atom as A.

  - All atoms or groups of atoms bonded to that central atom through the same electron domain will be called X.

  - All lone pair valence electrons on that atom will be defined as E.

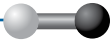
- To start, let's limit our discussion to molecules with a central atom from the second row. When we use this notation, we find that molecules with central atoms from row 2, only being able to hold 8 valence electrons, only have 4 possible situations.

- The elements in row 2 are limited by the fact that their valence shell can only hold 8 electrons. Only these geometries are possible; there are no exceptions.

Diatomic Electron Domain

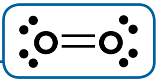
DOMAIN GEOMETRY

linear

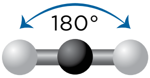
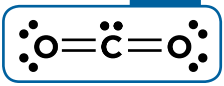


EXAMPLE

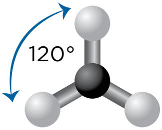
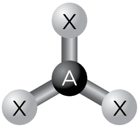
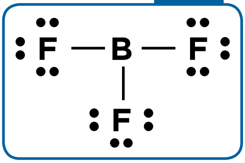
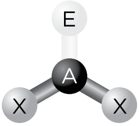
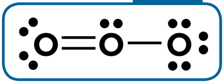
O_2



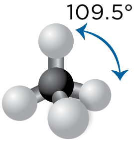
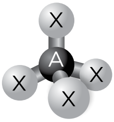
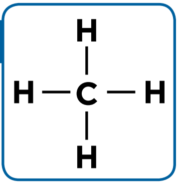
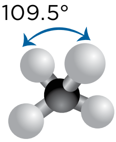
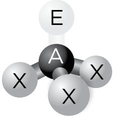
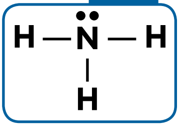
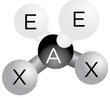
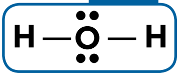
2 Electron Domains

DOMAIN GEOMETRY	SHAPE	FORMULA	MOLECULAR GEOMETRY	EXAMPLE
linear  	 	AX_2E_0	**linear**	**CO_2** 

3 Electron Domains

DOMAIN GEOMETRY	SHAPE	FORMULA	MOLECULAR GEOMETRY	EXAMPLE
trigonal planar  	 	AX_3E_0	**trigonal planar**	**BF_3** 
	 	AX_2E_1	**bent**	**O_3** 

4 Electron Domains

DOMAIN GEOMETRY	SHAPE	FORMULA	MOLECULAR GEOMETRY	EXAMPLE
tetrahedral  	 	AX_4E_0	**tetrahedral**	**CH_4** 
 	 	AX_3E_1	**trigonal pyramidal**	**NH_3** 
	 	AX_2E_2	**bent**	**H_2O** 

- But what happens when we use a different central atom, such as one from row 3 or beyond? For example, cisplatin is an anticancer drug that depends heavily on the molecule's shape for its efficacy. Its shape holds its 2 chlorine atoms at a 90° angle to the central platinum atom—perfectly in place to react with 2 neighboring nucleic acid bases within the DNA of a cancer cell.

- When these 2 chlorine atoms are replaced by bonds to specific atoms in the DNA, the DNA becomes kinked and therefore does not function properly. A subsequent cascade of complex chemical events ultimately leads to cell death, but it all starts when cisplatin makes that connection and kinks the DNA.

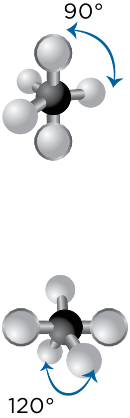
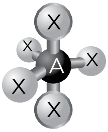
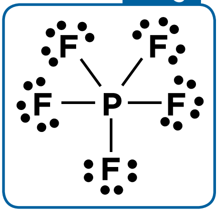
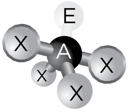
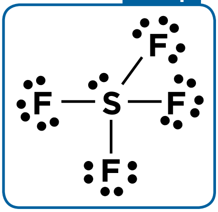
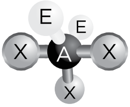
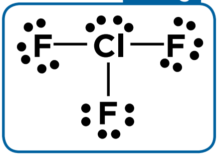
- If cisplatin had only 4 electron domains, we would expect it to look tetrahedral, like the AX_4 model, having bond angles of 109.5°—yet it is clearly not tetrahedral. This would put the chlorine atoms too far apart for the drug to function. So, what is going on?

- The secret to this new geometry is that elements from the third row and beyond, like platinum, have the ability to hold more than 8 valence electrons because they have a nearby *d* sublevel available. In most cases, this allows one or 2 additional pairs of electrons to be on the central atom in an apparent violation of the octet rule.

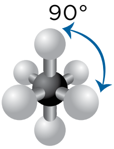
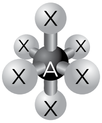
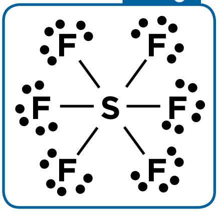
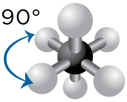
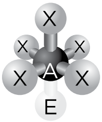
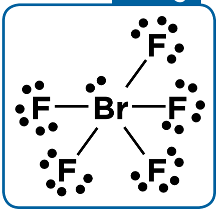
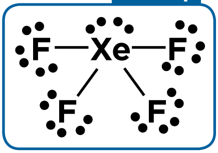
- So, armed with cisplatin's Lewis structure, we can begin to understand its peculiar geometry. But to do so, we first have to consider the possible geometries of molecules with expanded octets on their central atoms.

- Applying VSEPR theory allows us to explain and even predict the geometric arrangement of atoms in relatively simple molecules, from the methane found in natural gas to the geometry of anticancer drug molecules like cisplatin.

5 Electron Domains

DOMAIN GEOMETRY	SHAPE	FORMULA	MOLECULAR GEOMETRY	EXAMPLE
trigonal bipyramidal 		AX_5E_0	**trigonal bipyramidal**	**PF_5** 
		AX_4E_1	**see-saw**	**SF_4** 
		AX_3E_2	**T-shaped**	**ClF_3** 

6 Electron Domains

DOMAIN GEOMETRY	SHAPE	FORMULA	MOLECULAR GEOMETRY	EXAMPLE
octahedral  		AX_6E_0	**octahedral**	**SF_6** 
		AX_5E_1	**square pyramidal**	**BrF_5** 
		AX_4E_2	**square planar**	**XeF_4** 

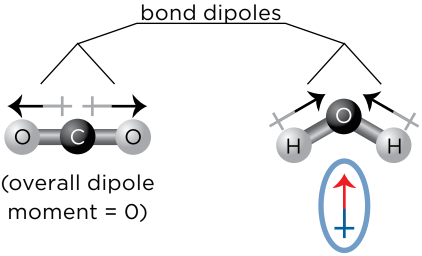
GEOMETRY AND POLARITY

- In addition to having a profound influence on the chemical properties of compounds, such as in the case of cisplatin, the geometric arrangement of atoms helps predict and explain some of the most fundamental properties of everyday materials, such as water and carbon dioxide.

- Water is commonly found as a liquid capable of dissolving a variety of salts that form ions in solution. The polar covalent oxygen-hydrogen bonds in water each have a partial charge separation. And the fact that water is an AX_2E_2 molecule means that it has a bent geometry.

- This means that the molecule itself has a more positive region and a more negative region of its electron cloud. If the oxygen-hydrogen bonds pointed in opposite directions, their dipoles would cancel over the molecule, but they don't.

- Carbon dioxide's polar carbon-oxygen double bonds are aligned opposed to one another. This means that, overall, there is no molecular dipole to CO_2.



- So, water is a polar molecule, and CO_2 is a nonpolar molecule. We know this from their molecular geometries. Why is this so important?

- Molecules with strong permanent dipoles can align themselves so that the dipole of one molecule interacts favorably with the dipole of its neighbor. Just as the magnetic dipoles in magnets can make them prone to sticking together, the electrostatic dipole of polar molecules can cause them to stick together better when aligned properly.

- It is this ability of water molecules to attract one another and stick together that gives them the ability to remain liquid or solid at temperatures necessary for life.

- If water were instead linear, having no dipole, it would probably have properties more closely resembling carbon dioxide, which, just like water, contains 3 atoms, with 2 highly polar bonds joining them, but is a gas at all but the most frigid temperatures and even when liquefied cannot dissolve salts the way water can.

- So, this simple geometric feature, a slight bend in the water molecule, is all that stands between a planet like Earth, being covered by oceans and glaciers, and one in which water would most likely only be found in the atmosphere, if at all. It would be a radically different environment, all caused by one simple bend in one of the simplest molecules imaginable.

- We can use this technique to analyze the polarity of just about any small molecule that we want—by first determining the electron domain geometry, then determining the molecular geometry of the molecule, and finally considering if the individual bond dipoles within the molecule cancel or not.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 345–360.

UC Davis ChemWiki, “VSEPR.”
http://chemwiki.ucdavis.edu/Core/Inorganic_Chemistry/Molecular_Geometry/VSEPR.

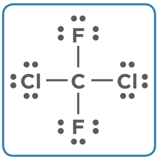
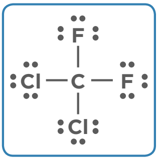
QUESTIONS

1 If lone pair electrons push slightly harder against others than bonding pairs do, how might this subtly affect the magnitude of the bond angles in compounds like water that have 2 of each type of electron pair on their central atom?

2 Knowing how like and opposite charges interact, why might it be useful to know if a small molecule is polar or not?

3 Freon-12 is a version of Freon with the formula CF_2Cl_2. Draw the Lewis structure for Freon-12. Is this molecule polar?

Answer

3)  or 

(both Lewis structures are correct).
This molecule is polar, because the tetrahedral geometry leads to bond dipoles that do not cancel out completely.

Hybridization of Orbitals

LECTURE 12

In this lecture, you will endeavor to understand the apparent conflict between the electronic structure of individual atoms and of those that are bonded to others. You will learn how legendary physical chemist Linus Pauling brought his intellect to bear on this problem, formulating a theory of orbital hybridization. You will explore how this elegantly simple concept helped to further bridge the gap between our understanding of the structure of atoms and the structure of molecules.

PAULING'S THEORY OF ORBITAL HYBRIDIZATION

- American-born chemist Linus Pauling found that most long-used theoretical estimates of bond lengths and angles in the 1930s were simply wrong. The bonding theories of the day did not match his findings when he applied new X-ray technology to old problems.

- So, Pauling contemplated a disconnect in our understanding at the most basic chemical level—that of bonding. He had to find a way to explain the discrepancy between the old and new understanding of how molecules were put together.

- One of the fundamental issues with which Pauling was struggling was that methane—one of the simplest molecules known to exist, with just one central carbon surrounded by 4 hydrogen atoms—forms a perfect tetrahedral molecule in which all 4 carbon-hydrogen bonds are identical. Every probe available to Pauling told him that methane has only one type of carbon-hydrogen bond—all identical in every way.

- But the central carbon has 2 distinct types of valence electrons: 2*s* electrons and 2*p* electrons. If covalent bonding were taking place by the overlap of atomic orbitals in carbon with the *s* orbitals of hydrogen atoms, shouldn't there be 2 different types of carbon-hydrogen bonds in methane, one resulting from the overlap of a hydrogen's *s* orbital with a carbon *s* orbital and another resulting from the overlap of a hydrogen *s* orbital with one of the carbon's *p* orbitals?

- Pauling was faced with a serious problem. The Rutherford atom was well characterized and clearly showed that isolated carbon atoms have 2 different types of valence electrons. Yet VSEPR theory properly predicted the tetrahedral geometry of methane with 4 equivalent bonds. The 2 theories were not consistent with one another.

- Was one of these theories wrong, or was there something more going on when atoms formed bonds? Was there some sort of fundamental geometric change that atomic orbitals underwent when forming the bonds that hold molecules together?

- Pauling suggested that orbitals themselves could combine and change as bonding takes place in a process that he called hybridization. His idea was that when an atom bonds, its valence orbitals can combine and average out to form any number of identical orbitals needed for bonding. It was not only a stroke of genius, but it also won Pauling a Nobel Prize in Chemistry.

AVERAGING

- When it comes to the hybridization of orbitals, multiple atomic orbitals can be grouped, blended together, and then divided into equal parts to create a new set of orbitals with new properties that are sort of a weighted average of those that went in.

- Let's analyze the electronic structure of a carbon atom in terms of energy. The valence shell of a carbon atom contains 1 2*s* orbital and 3 2*p* orbitals. Carbon's ground state configuration—the lowest energy arrangement of electrons that it can have—is $1s^2\ 2s^2\ 2p^2$. But an orbital can only hold 2 electrons at most, so the 2*s* electron pair must be separated to properly prepare the carbon to bond with 4 hydrogen atoms.

- This means promoting an *s* electron into a *p* orbital, which will require some energy input because 2*p* orbitals are higher in energy than 2*s* orbitals.

- If the structure of the orbitals on the central carbon atom did not change during the bonding process, we would expect to have one bond to hydrogen made through a carbon *s* orbital and 3 bonds to hydrogen through overlapping *p* orbitals.

- But Pauling's theory predicted that atomic orbitals will produce equal portions that are identical in composition when bonding: 1 *s* orbital and 3 *p* orbitals combine, or hybridize, to form 4 new orbitals that are ¼ *s* in character and ¾ *p* in character. As this takes place, their energies change slightly, becoming a bit higher in energy than an *s* orbital but a bit lower in energy than a *p* orbital.

- This process doesn't only change their relative stability, either. It also changes their shapes into something resembling a combination of *s* and *p* orbitals: a dumbbell, which is slightly elongated on one side and slightly smaller on the other.

- Pauling's ingenious theory allows us to finally explain how it is possible that atoms with different sublevels of their valence shell can form many identical bonds to multiple atoms.

- And hybridization does not have to stop with *s* and *p* orbitals. The number of atomic orbitals in must equal the number of atomic orbitals out, so elements from the third row of the table can take on even more valence electrons during bonding, bringing some of their *d* orbitals into the hybridized set.

- This leads to the potential for hybridization states like sp^3d and sp^3d^2, which correspond to trigonal bipyramidal and octahedral electron domain geometries.

- You may also notice that *d* orbitals, although they are all exactly the same energy, are not all exactly the same shape the way that *p* orbitals are, offering us an explanation for the unusual trigonal bipyramidal geometry that has 2 different sets of bond angles. So, Pauling's tinkering hasn't just allowed us to unify the Rutherford atom with VSEPR theory, but it also cleans it up a bit.

DETERMINING THE HYBRIDIZATION STATE OF AN ATOM

- Sigma bonds form directly in between nuclei. This means that, in most cases, hybrid orbitals are good at forming sigma bonds, because they have some *s* orbital character. Lone pairs aren't involved in bonding, but they prefer to be in the lowest possible energy state that they can. Again, usually this means a hybrid orbital. So, sigma bonds and valence shell lone pairs tend to be found in hybrid orbitals.

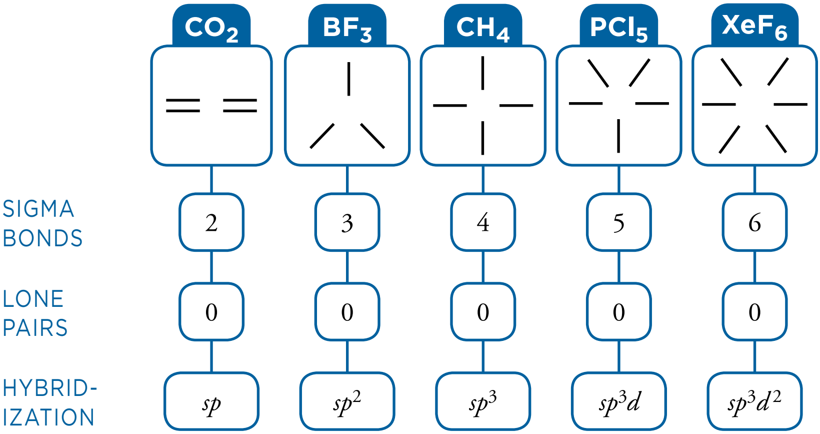
- But pi bonds—the bonds that make up the second and third bonds in multiple bonds—behave differently. Pi bonds form by the side-to-side overlap of unhybridized *p* orbitals. Because hybridization changes the shape of orbitals and makes them less symmetrical, hybrid orbitals can't form pi bonds.

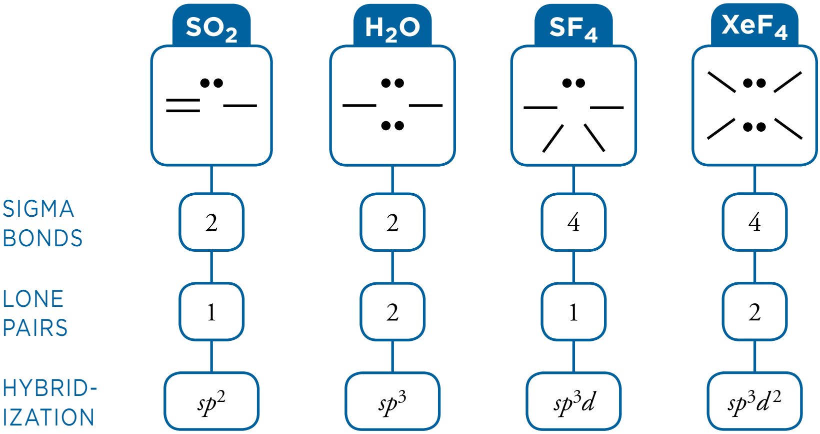
- Once we understand the energetics behind hybrid orbital theory, we can more quickly determine the hybridization state of an atom, simply by counting sigma bonds and lone pairs.

- We can use the Lewis structure of some simple molecules, such as carbon dioxide, to determine their hybridization state. We can leave out the lone pair electrons on the central atom because they are of no consequence to the hybridization state of the central atom.

- Hybridization states of central atoms can be determined from 2 important pieces of information: the number of sigma bonds and the number of lone pairs. We can combine that information to determine hybridization states.

- For example, for carbon dioxide, we have 2 electron domains. Both of them are bonding. That means that the first bonds in the double bonds are sigma bonds. They go into hybrid orbitals. But the other bonds, the second bonds in the double bonds, are not in hybrid orbitals; instead, they are in unhybridized *p* orbitals. So, we have 2 sigma bonds.





EXAMPLE FROM NATURE

- Understanding hybridization of orbitals is a crucial underpinning to our understanding of molecular geometries. The shape of a molecule—the geometric arrangement of the atoms that make it up—can be every bit as influential in determining the properties of a compound as the identities of the elements making it up.

- The world is filled with examples of this. One connection between hybridization states of atoms and everyday life is the need to have phosphorus in our diets. The human body is made primarily of oxygen, carbon, hydrogen, and nitrogen. All of these elements hail from the first 2 rows of the periodic table and therefore do not have access to *d* orbitals to take on more complex hybridization states.

- But not much farther down the list are elements like sulfur and phosphorus. Phosphorus is a part of the glue that holds some of the most critical molecules in biochemistry together. Take the example of ribonucleic acid (RNA), the chemical cousin of DNA that, among other things, plays a role in converting information in our genes into useful molecules that our bodies rely on to function.

- Phosphorus holds individual nucleic acids together through a bond known as a phosphate ester. Phosphate esters are pretty tough, and they can keep molecules like RNA and DNA intact pretty well. But when the time comes that your body needs to break down RNA to build new messenger molecules, it needs a way to break those bonds and disassemble the RNA.

- As the bond holding ribonucleic acids is broken, the phosphorus in the backbone changes its hybridization state from sp^3 to sp^3d, allowing the reaction to take place. Place a different atom there, even a chemical cousin from the same group, and the properties of that system would change so drastically that it would be unusable in a living organism.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 360–373.
Cobb and Goldwhite, *Creations of Fire*, pp. 327–328.

QUESTIONS

1 Is it theoretically possible to have hybrid orbitals that include *f* atomic orbitals? If so, which elements might be capable of including such atomic orbitals in their hybridization behavior?

2 We focused on the hybridization states of central atoms in small molecules in this lecture. Are the exterior atoms of the molecules that were discussed in this lecture hybridized as well? If so, what are their hybridization states?

3 Silane (SiH_4) is a compound used in some water repellents. What is the hybridization state of the central atom in this compound?

Answer

The silicon atom in silane has 4 bonding electron pairs and no lone pairs, so it is sp^3 hybridized.

Molecular Orbital Theory

LECTURE 13

As useful as valence bond theory, VSEPR, and hybridization theory are in predicting the properties of substances, they can all be put to shame using one of the simplest molecules: oxygen. In many ways, oxygen behaves itself in the face of these theories. It contains the double bond predicted by valence bond theory. Its atoms have no formal charge, just as its Lewis structure would predict. In addition, the bond length and strength between the 2 oxygen atoms is consistent with Pauling's measurements and hybridization theory. But oxygen has one property that can't be explained by any of these: It is attracted to magnets. It is this property that spurred the molecular orbital theory.

MOLECULAR ORBITAL THEORY

› Oxygen is one of a class of materials called paramagnetic materials. Probably the most familiar material with this property is metallic iron. Take a sample of iron and place it near a magnet. That sample is attracted by the magnet.

› Paramagnetic materials like iron are attracted to magnetic fields because of unpaired electrons in their electron clouds. This is easily explained in the case of iron because the 3*d* electrons in the electron cloud of an iron atom are unpaired. This is in accordance with Hund's rule, which dictates that degenerate electrons must occupy their own orbital whenever possible.

› The paramagnetic nature of iron is no mystery to us, but in 1847, famed researcher Michael Faraday reported a strange observation—that oxygen was also attracted to magnetic fields, just like iron. Oxygen is paramagnetic, which means that although it has no permanent magnetic field of its own, it is attracted to other permanently magnetized objects.

- We reach an inescapable conclusion in the face of this observation. Oxygen must have unpaired electrons. This probably didn't vex Faraday much, because he couldn't have postulated this—the electron itself hadn't yet been discovered.

- But as our understanding of atomic and molecular structure advanced even further through the early 1900s, it became clearer that unpaired electrons were almost always found in paramagnetic materials.

- In every Lewis structure of oxygen we have drawn so far, there has never been any indication of an electron without a partner. Based on everything we know now, oxygen should not have this property. So, what is going on?

- Remarkably, the answer to that question would have to wait until 1933, when Friedrich Hund and Robert Mulliken brought their intellect to bear on the problem. Hund and Mulliken had asked an even simpler question: If electrons can exchange places within an atom's electron cloud as hybridization theory requires, can they exchange places within a molecule as well? In other words, is it possible that an electron in a molecule could move through larger regions defined by combinations of overlapping atomic orbitals?

- They found that the answer is yes, and they dubbed these larger combined spaces molecular orbitals. This expansion of hybridization theory would be bound by some of the same rules—most notably that the number of atomic orbitals in equals the number of molecular orbitals out.

- But unlike hybridization theory, not all molecular orbitals are of the same energy. When adding atomic orbitals together across entire molecules, the complex geometric overlapping that takes place creates a set of molecular orbitals that can be very different from one another.

- These new molecular orbitals vary in energy. Some are lower in energy than the contributing atomic orbitals and are called bonding molecular orbitals. They are usually indicated by the Greek characters sigma (σ), pi (π), and delta (δ) to keep in line with atomic orbital notations *s*, *p*, and *d*.

- Some molecular orbitals are equal in energy to the contributing atomic orbitals. So, there is no benefit or penalty to placing electrons in them. These molecular orbitals are called nonbonding molecular orbitals.

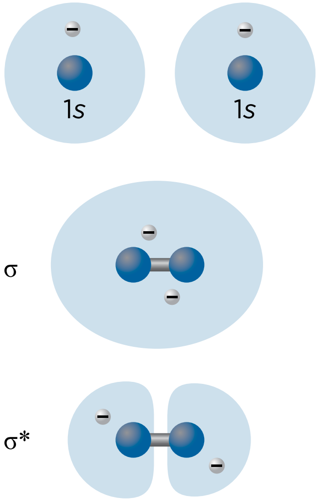
- The third type of molecular orbitals that can form are higher in energy than their atomic orbital counterparts. Because there is an energetic penalty to populating them with electrons, they are called antibonding orbitals. They are labelled sigma star (σ*), pi star (π*), and so on.

MOLECULAR ORBITALS OF HYDROGEN

- Consider the simplest molecule: H_2, the dihydrogen molecule. To create the molecular orbitals, let's first think of these hydrogen atoms as being separate from one another. They haven't bonded yet, which means that each of these hydrogen atoms has a 1*s* subshell with a single electron in it.

- When we put those 2 hydrogen atoms together, molecular orbital theory tells us that the orbitals should combine in a way that creates a more stable system overall—a molecular orbital that's more stable than isolated hydrogen orbitals would be.

- The molecular orbital is more stable when hydrogens are bonded because, due to the shape of the construct that forms, there's going to be more electron density in the center of that molecule—in between the 2 hydrogen nuclei, sort of screening them from one another. This lowers the overall energy of this particular pair of electrons.

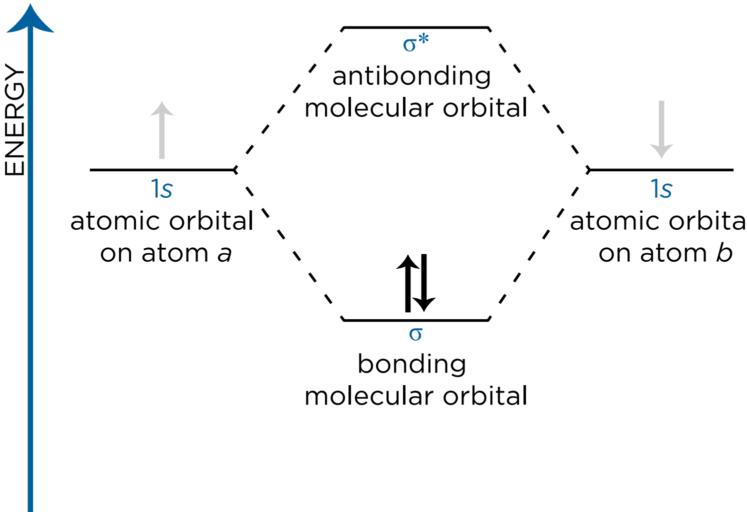


- There's also a second molecular orbital that forms. Remember that we always count up all the atomic orbitals in and get an equal number of molecular orbitals out. The second one is not a sigma, but a sigma star.

- In the second way that these *s* subshells can combine, there is a plane through the middle where there's almost no electron density, if any at all. That means those electrons spend more time outside of the H_2, so they're not screening those nuclei from one another. They're not making it more stable; in fact, they're making it less stable. If electrons occupy this so-called sigma star molecular orbital, they will actually destabilize the bond, making it worse than not being bonded at all.

- Each atomic orbital of hydrogen has a single electron in it—the 1*s* electrons. The energy of those orbitals is equal to the nonbonded energy. That means that anything that forms that's lower in energy is going to be a bonding molecular orbital, whereas any orbital that forms that's higher in energy is going to be an antibonding molecular orbital.

- Our job is to use the inventory of electrons afforded to us in the 2 hydrogen atoms to fill the molecular orbital system, and ask one very important question: Does it lower the overall energy of the system? If so, a bond will form.



- The overall energy of the system decreases as a result of populating the molecular orbitals. Therefore, a bond will form. Furthermore, we can count the multiplicity of the bond. The bond order in any molecule is calculated using the number of bonding electrons and the number of antibonding electrons.

- In this case, we have 2 bonding electrons. We have 0 antibonding electrons for a balance of 2, and remembering that it takes 2 electrons to form a bond, the following equation tells us exactly what the bond order should be:

$$\text{bond order} = \left(\frac{\text{bonding electrons} - \text{antibonding electrons}}{2}\right).$$

  In this case, the bond order is 1. Therefore, the molecular orbital diagram predicts that hydrogen will exist as a diatomic molecule with a single bond, and that is exactly what we see.

- Molecular orbital theory correctly predicts that hydrogen will be diatomic, or a molecule consisting of 2 covalently bonded atoms. It also predicts that helium will be monatomic, existing as an isolated atom. It can also demonstrate that fluorine should be a diatomic molecule with a single bond joining the 2 fluorine atoms.

- But the octet rule and valence bond theory already predicted this. So far, Hund and Mulliken's work hasn't contributed anything new except for a different way of thinking about what was already known at that time.

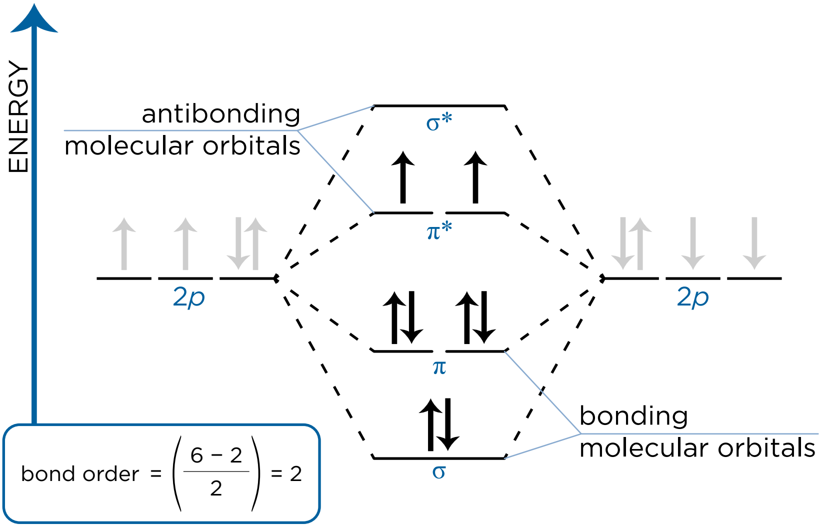
- But the real advantage of molecular orbital theory becomes clear when we turn our attention to oxygen—a molecule that so far has never appeared in this course as a molecule with unpaired electrons. No lens through which we have looked to date can explain why oxygen gas is attracted to a magnet. But we now have a new lens: molecular orbital theory.

MOLECULAR ORBITALS OF OXYGEN

- Consider the molecular orbitals of a dioxygen molecule, O_2. This is going to involve the *p* subshells of oxygen. Oxygen is a $2p^4$ element, so we're going to have a total of 8 electrons to populate this molecular orbital system. When we follow Hund's rule and the Pauli exclusion principle and try to find the most stable configuration, we're going to be able to put 6 of those electrons into bonding molecular orbitals, and that has the effect of lowering the energy overall.

- In the case of oxygen, we have 2 electrons left, and we need to put them somewhere. Naturally, they'll go into the pi star system—but how will they arrange themselves? This is the important question.

- Remember that Hund's rule says that we want to maximize spin, and the Pauli exclusion principle says that we can't necessarily have 2 electrons with exactly the same 4 quantum numbers and atoms, and the same thing applies here. In other words, we can't put them both in the same orbital with the same spin. So, to satisfy both of these rules, we have to put them in separate pi star molecular orbitals.



$$\text{bond order} = \left(\frac{6-2}{2}\right) = 2$$

- Both electrons have the same spin, so spin is maximized, and they are not in the same orbital. That's going to counter a little bit of the effect of the bonding molecular orbitals, so we have a situation where 6 bonding electrons are going to be cancelled out only by 2 antibonding electrons, giving us a total bond order of 2, which we've come to expect from oxygen. But even more importantly than that, it explains oxygen's magnetic behavior—something that no previous technique could do.

MULLIKEN VERSUS PAULING

- Mulliken was molecular orbital theory's greatest champion, and one of his most epic sparring matches over the nature of the chemical bond was with the man who conceived its predecessor, hybridization theory: Linus Pauling. Mulliken and Pauling famously took jabs at one another's theories in the literature of their day, each championing his own model of the chemical bond as the correct one.

- Of course, the truth is much clearer to chemists today—that both of these theories are just models. Each predicts the behavior of certain systems better in certain circumstances. In hindsight, today's chemist can look back on this chapter of chemical history and clearly see how Hund and Mulliken's creation expanded our understanding of molecular systems. It wasn't just its ability to explain the magnetic behavior of oxygen; it was also remarkably adept at explaining the properties of larger molecules, which Pauling's hybridization theory could not.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 373–386.
Cobb and Goldwhite, *Creations of Fire*, pages 329–331.

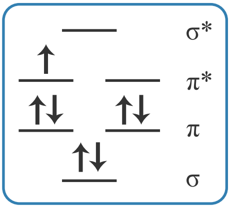
QUESTIONS

1 How might the molecular orbital diagram for a heteronuclear diatomic molecule (a molecule consisting of 2 different atoms), such as HF, differ from the homonuclear systems that were discussed in this lecture?

2 Molecular theory can be used to analyze not only neutral molecules, but also ions. Use the molecular orbital diagram for the oxygen molecule to determine the bond order in an O_2^+ ion (an O_2 molecule that has lost an electron).

Answer

2)



(6 – 1)/2 = 2.5.

The bond order of O_2^+ is 2.5.

Communicating Chemical Reactions

LECTURE 14

The topic of this lecture is chemical reactions—the processes in which chemical bonds between and among atoms are broken, formed, and rearranged to convert one material into another. You will learn how to represent a chemical reaction in a condensed, concise way. You will also learn how complex mechanisms might be hiding behind those simple recipes for chemical change. Furthermore, you will learn how to classify some of the reactions that you will encounter in this lecture and how to calculate the molar mass of a molecule.

DEFINING A CHEMICAL REACTION

› A chemical reaction is any process that results in the breaking, formation, or rearrangement of chemical bonds. Processes like melting ice or boiling water are not considered chemical changes. During these kinds of processes, the bonds within molecules are unaffected.

› Water molecules can be a part of solids, as in ice; liquids, as in liquid water; or gases, as in steam or water vapor. But the molecules making up each of these materials have exactly the same structure: 2 hydrogen atoms bonded to a central oxygen in a bent geometry. So, changing ice to liquid water or liquid water to steam doesn't count as a chemical reaction. In fact, changes like melting and boiling can be called physical changes to distinguish them from chemical changes.

› Additionally, processes that change the identities of atoms themselves are not chemical reactions. Radioactive decay, which causes a uranium atom to convert into lead, can't be considered a chemical reaction, because the element's identity itself is changed. We also can't classify the fusion that goes on in the Sun as chemical in nature, because smaller atoms are being combined to create new elements—for example, 2 hydrogen atoms combining to form one helium atom. Again, atoms are changing their own makeup. This would instead be called a nuclear reaction.

- Chemical reactions can be thought of as bridging the gap between physical changes and nuclear reactions—at least in the sense of scale. Physical changes involve the separation or conglomeration of intact molecules. Nuclear reactions involve the separation or combination of atomic nuclei.

- But chemical reactions take place between that—at the bond level. They happen when the electrons holding molecules together relocate, breaking old bonds and forming new ones. Molecules themselves are pulled apart or conjoined without disrupting the nuclear structure of each atom involved. When this happens, what we begin with is called starting materials, reactants, or sometimes reagents, and what we get out of the process is called the product of the chemical reaction.

- This definition may seem a bit narrow, but processes that fit this mold are going on all around us every minute of every day.
    - Carbon dioxide emissions from vehicles and biological sources are reacting with water in the air to become carbonic acid, a weakly acidic substance that makes rainwater slightly acidic.

    - At home, in your favorite bottle of wine, a compound called sodium metabisulfite is breaking down slowly into sodium bisulfite, an ionic compound that is toxic to the naturally occurring bacteria in wine that want to turn it into vinegar to support their own biological needs.

    - Tarnished silverware can be cleaned using aluminum foil under the right conditions, under which silver sulfide and aluminum react to become aluminum sulfide and pure silver.

    - Steel is a crucial commodity in commerce and construction. After molding, though, it commonly has a tough outer scale of iron oxide. This layer is commonly cleaned using hydrochloric acid in a chemical reaction called pickling of the steel.

- All of these processes constitute chemical reactions because the bonding of atoms is changing. Whether we are building molecules, breaking them down, or modifying them, they all meet the crucial criteria of bond alteration.

DRAWING CHEMICAL REACTIONS

- Just as chemists have systems for depicting the molecular formulas or Lewis structures of a compound, they have a shorthand system to convey the conversion of one set of compounds to another. A generic chemical reaction can be written as follows:

$$X_A \text{ reagent A}_{\text{(phase)}} + X_B \text{ reagent B}_{\text{(phase)}} \rightarrow$$
$$X_C \text{ product C}_{\text{(phase)}} + X_D \text{ product D}_{\text{(phase)}}$$

- The reactants, or reagents, are on the left side of the equation, and they each have a coefficient that tells us how much of each of the reagents we start with. The products are on the right side of the equation, and they each have a coefficient that tells us how much of each of the products will form. The phase—whether it is a solid, liquid, or gas—is also indicated.

- The combustion of propane is the reaction that creates the energy that powers your barbecue grill or furnace. One of the reagents of this reaction is propane, or C_3H_8. In addition, any combustion reaction involves oxygen. The combustion of propane creates 2 products: carbon dioxide and water. This reaction will carry out completely in the gas phase, so we can use the notation for gas, (g), on all of the reagents and products.

$$1\ C_3H_{8\ (g)} + 5\ O_{2\ (g)} \quad 3\ CO_{2\ (g)} + 4\ H_2O_{\ (g)}$$

- The coefficients tell us how much propane will react and how much carbon dioxide will form, for example. Specifically, when we react 1 mole of propane gas with oxygen in combustion, it will consume 5 moles of oxygen and, in doing so, will produce 3 moles of carbon dioxide and 4 moles of water. This is a completed chemical reaction in which we know not only the identities, but also the phase and the quantity of all the reagents and products that will form and be consumed.

- A chemical reaction is like a recipe for changing a set of ingredients (called reactants) into a finished dish (called a product)—at least in the sense that we know how much of each reactant combines and how much product will be created when they do.

- But there is more to a recipe than just a list of ingredients. Recipes often require that we combine the ingredients in a stepwise fashion. Chemical reactions often take place in steps, with intermediates forming and reacting further as the reaction proceeds. This more detailed description of a reaction is called its mechanism.

- For example, when we react 2 moles of nitrogen oxide (NO) gas with 1 mole of oxygen gas to form 2 moles of nitrogen dioxide (NO_2), this reaction doesn't take place in a single step. Instead, it takes place in a stepwise fashion.

$$2\,NO_{(g)} + O_{2\,(g)} \rightarrow 2\,NO_{2\,(g)}$$

- In this case, we've written the reaction as though 2 moles of NO and 1 mole of O_2 simply collide and come out the other side as products. But that's actually not what happens. Instead of having all 3 molecules collide and react simultaneously, there's a stepwise process to building it up.

- In terms of the mechanism of this reaction, the first step is the reaction of the 2 moles of NO gas to form N_2O_2, which is an intermediate. Next, the intermediate itself reacts in a subsequent step. In this case, the intermediate reacts with the remaining reagent, oxygen. When these 2 molecules collide and react, they create the final product.

$$2\,NO_{(g)} + O_{2\,(g)} \rightarrow 2\,NO_{2\,(g)}$$

$$2\,NO_{(g)} \rightarrow \cancel{N_2O_{2\,(g)}}$$

$$\cancel{N_2O_{2\,(g)}} + O_{2\,(g)} \rightarrow 2\,NO_{2\,(g)}$$

BASIC CLASSES OF CHEMICAL REACTIONS

- With a vast library of substances that can potentially be interconverted at the chemical level, we will never run out of new reactions to study. In fact, the sheer number of possibilities might be a bit overwhelming to the uninitiated.

- In truth, it can be overwhelming even to the highly trained, so chemists have devised ways to categorize chemical reactions. This helps us better understand chemical reactions by making us reflect on their similarities and differences—thinking of all the amazing reactions that we study not as isolated cases, but in more basic terms.

- There are many ways to classify chemical reactions, but the most general system consists of 4 simple types of chemical changes: synthesis, decomposition, single displacement, and double displacement.
  - Synthesis takes place when 2 or more smaller reagents combine to form a single larger product.

  - Decomposition can be thought of as the reverse of synthesis, or a process in which larger starting materials are broken down into smaller and more numerous products.

  - Single displacement can be thought of as a combination of synthesis and decomposition, in which one reactant replaces a part of another molecule, liberating that which it replaced.

  - In double displacement, sometimes also called metathesis, 2 or more reactants exchange a portion of themselves with one another.

- An example of a synthesis reaction is the formation of carbonic acid from water and carbon dioxide. This environmentally critical reaction is a synthesis because it combines 2 molecules, water and carbon dioxide, to make a larger compound, carbonic acid.

- The breakdown of sodium metabisulfite into sodium bisulfite is classified as decomposition. This is because a larger reactant, sodium metabisulfite, breaks down into 2 smaller products, sodium bisulfites.

- A single displacement occurs when you give silver sulfide a chance to react with aluminum metal. The aluminum takes silver's place in the ionic compound while the silver becomes pure metal. Essentially, one pure material switches places with another.

- The central reaction used in the pickling of steel is a perfect example of a double-displacement reaction, because iron in combination with oxygen reacts with hydrogen in combination with chlorine to form products in which both species exchange a partner.

- There are many ways to consider and characterize reactions, and this system of thinking is just one of them.

MOLAR MASS

- Chemical reactions can be used as a tool to design and even predict the results of chemical reactions that we can use in the lab, manufacturing plants, and elsewhere. Reactions are written out using coefficients to indicate the number of moles of each reactant and product consumed and formed, respectively. But we want to use chemistry in the real world, where researchers, manufacturing technicians, and chefs don't count molecules.

- The idea might seem a bit absurd. How can we count molecules that we can't even see, let alone count enough to be a meaningful quantity? Counting a trillion trillion invisible molecules to set up a chemical reaction simply isn't how we function. Instead, we measure quantities that can be determined using simple equipment quickly—such as mass, for example.

- But how do we use a recipe in moles to do business in grams? We have to do some unit conversion. One of the simplest forms of measurement that we can perform in the laboratory is the measurement of mass—weighing objects or samples. So how can we use such measurements to discuss chemical reactions?

- We turn to the periodic table to calculate molar mass, which can be calculated from the atomic masses of all the atoms comprising a particular molecule. The atomic mass in atomic mass units is equal to molar mass in grams. So, to determine molar mass, we inventory all of the atoms in a molecule and take the sum of the atomic masses. Molar mass can be converted from grams to moles or from moles to grams.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 80–84.

UC Davis ChemWiki, "3.7 Chemical Equations."
http://chemwiki.ucdavis.edu/Textbook_Maps/General_Chemistry_Textbook_Maps/Map%3A_Chemistry_(Zumdahl_and_Zumdahl)/03%3A_Stoichiometry/3.07_Chemical_Equations.

QUESTIONS

1 Consider the following reactions. To which class of chemical reaction does each belong?

a Limestone is made primarily of calcium carbonate. When heated, it reacts to form calcium oxide and carbon dioxide.

$$CaCO_3\ _{(s)} \rightarrow CaO\ _{(s)} + CO_2\ _{(g)}$$

b A hydrogen molecule reacts with oleic acid ($C_{18}H_{34}O_2$) to produce steric acid ($C_{18}H_{36}O_2$) in a process known as hydrogenation of oils.

$$C_{18}H_{34}O_2\ _{(l)} + H_2\ _{(g)} \rightarrow C_{18}H_{36}O_2\ _{(s)}$$

c Fluoride ion reacts with hydroxyapatite in your teeth to form hydroxide and fluorapatite, which strengthens tooth enamel.

$$F^-\ _{(aq)} + Ca_5(PO_4)_3OH\ _{(s)} \rightarrow OH^-\ _{(aq)} + Ca_5(PO_4)_3F\ _{(s)}$$

2 Write out a notation for a gas-phase reaction in which 1 mole of methane molecules react with 2 moles of oxygen molecules to produce 1 mole of carbon dioxide molecules and 2 moles of water vapor.

Answers

1a) decomposition; 1b) synthesis; 1c) single displacement;
2) $CH_{4\ (g)} + 2\ O_{2\ (g)} \rightarrow CO_{2\ (g)} + 2\ H_2O_{\ (g)}$.

Chemical Accounting: Stoichiometry

LECTURE 15

The coefficients of all reactants and products are carefully chosen to ensure that an equal number of each kind of atom appears on both sides of the equations. The relationship—the molar ratios of each reactant and product involved in a given reaction—is called that reaction's stoichiometry. When the coefficients properly account for this, a chemical equation is considered balanced. As you will learn in this lecture, balancing equations is a crucial skill, nearly as old as the science of chemistry itself and indispensable even in the most modern laboratories.

BALANCING CHEMICAL REACTIONS

- Balancing most chemical reactions relies on one very important rule: that reactions must be mass balanced. In other words, the same number of atoms that go in of each kind must come out at the end of the reaction. This was a critical rule in John Dalton formulating his atomic theory.

- The following is the combustion of propane without coefficients, where propane (C_3H_8) and oxygen (O_2) are the reagents and carbon dioxide (CO_2) and water (H_2O) are the products.

$$1\ C_3H_{8\ (g)} + 1\ O_{2\ (g)} \rightarrow 1\ CO_{2\ (g)} + 1\ H_2O_{\ (g)}$$

- To start, assuming that all reagents and products have coefficients of 1, we have one propane with 3 carbons in it, so we have 3 total carbons on the reactant side. We have 8 hydrogens and one oxygen molecule, giving us 2 atoms of oxygen. On the product side, 1 mole of CO_2 gives us 1 mole of carbon, and 1 mole of H_2O gives us 2 moles of hydrogen. The CO_2 and H_2O combined give us a total of 3 oxygens. Nothing is balanced.

- The next step in the process is to not change the pure elements until the very end—in this case, that's the oxygen in the reagents. Now we can start balancing various elements at will. Let's start by changing the carbon in CO_2 by changing its coefficient to 3. By tripling the magnitude of that coefficient, we're going to triple the amount of carbon, but we're also going to add additional oxygens—in this case, 4 more oxygens, for a total of 6 oxygens coming from CO_2. We have balanced carbon, but we still have 2 elements to worry about.

$$1\ C_3H_{8\ (g)} + 1\ O_{2\ (g)} \rightarrow 3\ CO_{2\ (g)} + 1\ H_2O_{\ (g)}$$

- Let's try to use water to balance out the hydrogen. Notice that we are deficient in hydrogen on products side, so let's increase the number of hydrogens by increasing the coefficient of H_2O to 4. In doing so, we're going to increase the number of hydrogens to 8, but we are also going to add additional oxygen atoms, bringing their total to 10 on the products side.

$$1\ C_3H_{8\ (g)} + 1\ O_{2\ (g)} \rightarrow 3\ CO_{2\ (g)} + 4\ H_2O_{\ (g)}$$

- Both carbon and hydrogen are balanced, but oxygen is still not balanced. But we have not tinkered with oxygen yet. Now we can change it and, in doing so, only alter the last ratio that's not quite right. To get the same number of oxygens on both sides, we simply change the coefficient on oxygen to 5, giving us 10 oxygen atoms. We have achieved balance, which means that we know exactly how much oxygen will react with exactly how much propane without running the reaction.

$$1\ C_3H_{8\ (g)} + 5\ O_{2\ (g)} \rightarrow 3\ CO_{2\ (g)} + 4\ H_2O_{\ (g)}$$

- In the lab, chemists don't sit at a microscope with tweezers counting the atoms of molecules. Instead, they like to measure in observable units, such as mass in grams. It seems that the problem is that quantities of reactants are measured in grams, but the reactions are governed by the ratios of molecules. But molar masses give us a way to navigate the gap between mass and number, and now that we have stoichiometry, we can analyze the economics of chemical reactions.

LIMITING REAGENTS

- One of the great uses of balanced chemical equations is in their ability to tell us how much of each chemical we need to complete a reaction on a given scale. When we have a reaction taking place between 2 or more reagents, the question of which will run out first always comes up. This is important to know, potentially for several reasons.

- We don't want to be wasteful with expensive materials, for example. Also, whichever is completely consumed first will dictate not only how much of the other reagent or reagents remain at the end of the reaction, but also the maximum amount of product that can form.

- The reagent we expect to be depleted first is called the limiting reagent for a given reaction, and the amount of product that can be produced by its complete consumption is called the theoretical yield of the reaction. We can determine the limiting reagent and theoretical yield of a reaction using the reaction's balanced chemical equation.

- When 1 gram of propane reacts with 2.5 grams of oxygen, which one is consumed first? The given information is in grams, which we can measure in the laboratory, but the reaction is balanced in moles. We have to find a way to jump back and forth between the values that we can measure in the lab and the values that the balanced reaction gives us.

$$1\ C_3H_{8\ (g)} + 5\ O_{2\ (g)} \rightarrow 3\ CO_{2\ (g)} + 4\ H_2O_{\ (g)}$$

- We start with the balanced equation. When 1 gram of propane reacts, how much oxygen would that gram consume. And do we have enough? A gram of propane isn't going to do us much good when all of our coefficients are in moles, but there is a way to get from grams to moles: molar mass. Keeping in mind that our target is grams of oxygen, we have to go through the stoichiometry first.

- We're going to use the molar mass of propane, which we can estimate at 44 grams per mole, but we divide through by that value because we want grams of propane to cancel. Now we're dealing with moles, which is great because our reaction stoichiometry tells us that 1 mole of propane will react with 5 moles of oxygen, and we can use that as a conversion factor. Setting it up as such, the moles of propane will cancel.

- Now we're working with oxygen. To make the final conversion of moles to grams of oxygen, we're going to use the molar mass of oxygen, which we can estimate at 32 grams per mole, and place it into the equation so that units cancel, leaving us with grams of O_2, the quantity that we want.

$$1.00\ \cancel{\text{g } C_3H_8} = \left(\frac{1\ \cancel{\text{mol } C_3H_8}}{44\ \cancel{\text{g } C_3H_8}}\right)\left(\frac{5\ \cancel{\text{mol } O_2}}{1\ \cancel{\text{mol } C_3H_8}}\right)\left(\frac{32\ \enclose{circle}{\text{g } O_2}}{1\ \cancel{\text{mol } O_2}}\right) = 3.64\ \enclose{circle}{\text{g } O_2}$$

- This calculation tells us that 1 gram of propane is going to need 3.64 grams of oxygen to completely react. Is oxygen limiting in this case? The problem gives us 2.5 grams, but we now know that we need 3.64 grams of oxygen, and because 2.5 grams is less than 3.64 grams, we now know that the oxygen is in fact limiting—it will run out before the propane does. Once we know which one of our reagents is limiting, we can determine the theoretical yield.

- To determine the theoretical yield, we're going to use the same quantities. Let's say that 1 gram of propane is going to react with 2.5 grams of oxygen, and we would like to know how much water that reaction will produce. The first piece of information we need is the limiting reagent, which we just discovered is the oxygen. We're going to begin with 2.5 grams of O_2, because this is the limiting reagent. It's going to run out first and stop the reaction when it's consumed.

- How many grams of water can we form from the reaction of 2.5 grams of oxygen? Keeping the starting and ending points in mind, let's set up an equation using our knowledge of molar masses and stoichiometry to get the answer.

- We're going to use the molar mass of oxygen first to get out of the realm of grams and into the realm of moles. We can estimate the molar mass of oxygen to be 32 grams per mole, and we divide through because we want the units to cancel properly. Now we're dealing with moles.

- The next step is to include the stoichiometry. In this case, because we properly balanced the reaction, we know that 4 moles of water are going to be produced when 5 moles of oxygen are reacted in a combustion reaction with propane. We can place these into the equation in such a way that moles of oxygen cancel.

- Once we're dealing with water, we want to get out of the realm of moles and back into grams. To do so, we're going to use water's molar mass, estimated at 18 grams per mole, and insert it into the equation in such a way that moles of water cancel, leading us to the unit that we want, grams of water.

- All that's left to do now is grab a calculator and run the math. When we do this, we discover that 1.13 grams of water will be produced when 2.50 grams of oxygen reacts completely in a combustion with propane.

$$2.50\,\cancel{\text{g O}_2} = \left(\frac{1\,\cancel{\text{mol O}_2}}{32\,\cancel{\text{g O}_2}}\right)\left(\frac{4\,\cancel{\text{mol H}_2\text{O}}}{5\,\cancel{\text{mol O}_2}}\right)\left(\frac{18\,\text{g H}_2\text{O}}{1\,\cancel{\text{mol H}_2\text{O}}}\right) = 1.13\,\text{g H}_2\text{O}$$

- If we wanted to verify this, we could simply run the same equation using our 1 gram of propane, setting up all of the terms so that we have appropriate cancelling. If an entire gram of propane were to combust, that would produce 1.64 grams of water. This is a validation of our selection of oxygen as a limiting reagent. This reaction will run until 1.3 grams of water is produced, at which time the oxygen will be fully consumed and the reaction will stop.

$$1.00\,\cancel{\text{g C}_3\text{H}_8} = \left(\frac{1\,\cancel{\text{mol C}_3\text{H}_8}}{44\,\cancel{\text{g C}_3\text{H}_8}}\right)\left(\frac{4\,\cancel{\text{mol H}_2\text{O}}}{1\,\cancel{\text{mol C}_3\text{H}_8}}\right)\left(\frac{18\,\text{g H}_2\text{O}}{1\,\cancel{\text{mol H}_2\text{O}}}\right) = 1.64\,\text{g H}_2\text{O}$$

- So, we were able to use a balanced chemical reaction to determine not only that oxygen is limiting, but also that exactly 1.13 grams of water should form if the reaction runs perfectly and to completion. But things in the lab rarely go perfectly. Some reactions don't run to completion. Others lose product mass to unwanted side reactions that produce by-products. Any number of things can cost us a portion of our products.

- So, chemists often report the yields of their reactions as a percentage of the theoretical yield. This is done by taking the actual yield of a reaction, dividing it by the theoretical yield, and multiplying by 100% to convert it into a percentage.

- For example, if our combustion reaction was found to produce 1 gram of water, that would be the actual yield. Compare this to the theoretical yield, and we find that we actually obtained 88.5% of what theory tells us.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 80–84.
Masterton and Hurley, *Chemistry*, 3.4.
UC Davis ChemWiki.
http://chemwiki.ucdavis.edu (search: "balancing equations").

QUESTIONS

1. Is it possible for an element to appear on just one side or the other of a chemical reaction?

2. We were careful to save the coefficients of pure elements as the last change during the balancing of a chemical equation. Is it possible for a chemical reaction to consist of reactants and products that are all pure elements? Is it possible for a chemical reaction to involve no pure elements?

3 What are the coefficients of each species in the following reaction when it is properly balanced?

$$KMnO_4 + HCl \rightarrow KCl + MnCl_2 + H_2O + Cl_2$$

Answer

3) $2\ KMnO_4 + 16\ HCl \rightarrow 2\ KCl + 2\ MnCl_2 + 8\ H_2O + 5\ Cl_2$.

Enthalpy and Calorimetry

LECTURE 16

In this lecture, you will begin to consider not just how some atoms and molecules can change and react with one another, but also how they can create, consume, and even transport possibly the most precious commodity in the universe: energy. The key to understanding the transfer and transformation of energy in the chemical world lies in 3 very simple rules that set the stage for a field of study known as thermodynamics. This lecture will focus on the first of these so-called laws of thermodynamics: Energy can be neither created nor destroyed.

MEASURING ENERGY

› Ancient civilizations knew how to coax energy from wood by burning it, and they knew that more fuel meant more energy. But the need to quantify exactly how much energy wasn't there until the Industrial Revolution came about. In the early 1800s, engineering and manufacturing advancements spurred the development of engines, electrical systems, and other devices that required very specific amounts of energy to be delivered in very specific ways.

› This new need to understand energy quantitatively drove a curious beer brewer named James Prescott Joule to take on a research project involving a new invention: the electric motor. Joule sensed an opportunity, noting that this new electric motor technology might be able to replace or outperform the steam engine technology that his brewery used in those days. He set out to study electrical energy.

- Joule knew that engines produced 2 things: heat and work. This is to say that they could impart a temperature change on their surroundings (usually an unwanted side effect), or they could physically move other objects by applying a force—the physical definition of work. Usually, these devices produce some of both.

- But Joule quickly noticed that there was an intimate relationship with the amount of work a system could do and the amount of heat it generated. Specifically, the more heat a device produced, the less work it could do per unit of fuel consumed.He observed that this was true regardless of the source of the energy. Steam, electrical, or otherwise, minimizing heat produced meant that a greater amount of work could be done by a device.

- Joule had made a revolutionary realization: He had realized that all energy is interrelated. Mechanical work and the generation of heat seemed to always balance out, meaning that they must be made of the same stuff—energy.

- Chemists and physicists uses Joule's name to dub the most fundamental unit of energy. A joule is the amount of kinetic energy imparted to an object when 1 newton of force acts on it over a 1-meter distance. In addition, 1 watt of power applied for 1 second transfers 1 joule of energy.

- There are a few other common units of energy, including the calorie. A calorie is equal to 4.17 joules and is the amount of energy needed to heat 1 gram of water by 1° centigrade. This is not to be confused with a food calorie, which is 1000 times larger than a simple calorie. Both of these units are the metric cousins of another well-known unit of energy, the Btu, or British thermal unit, which is the amount of heat needed to raise the temperature of 1 pound of water by 1° Fahrenheit.

- In theory, any one of these units is just as good as another. The Btu is very rarely called on in modern chemistry. There are chemists who choose to work in units of calories, but because of its more fundamental metric system foundations (newtons of force and meters of distance), the joule is by far the preferred unit of energy in chemistry.

HOW ENERGY MOVES

- The first law of thermodynamics tells us that energy can never be created or destroyed. It can only be exchanged. But exchanged between what? We can't talk about exchange without 2 discrete entities to participate in that transfer.

- The first order of business in any thermochemical experiment is to define 2 separate entities that do not mix: First, we define our system, which is usually the reacting matter that we want to study; and next, we identify the surroundings, which are technically all other matter in the universe.

- We can't really ever determine the absolute amount of energy contained in any chemical system, but we often can measure how its energy changes when chemical processes take place. So, we sometimes place a capital Greek delta (Δ)—a standard symbol meaning "change"—in front of terms like energy.

- Energy change is a 2-way street. Energy can flow from surroundings into a system or from a system into its surroundings. By convention, we always write these terms from the perspective of the system. So, if a system is losing energy, we use a negative sign (−) to demonstrate that the system's energy is decreasing. If, instead, a system is gaining energy, then we use a positive sign (+) to indicate that the energy is flowing into our system from the surroundings.

RELATING ENERGY, HEAT, AND WORK

- Energy is equal to heat plus work. This is to say that all of the energy in the universe is really only useful for 2 things: warming things up or pushing things around.

- The easiest way to determine the total amount of energy changing hands during a process is to carry out that process in such a way that no work is done. If that can be accomplished, then our equality simplifies: Heat and energy become equivalent.

ENTHALPY

- To begin understanding how chemists look at energy, we have to simplify things by eliminating work from the equation. We can do this by assuming that our chemical reaction does no work and takes place under conditions of constant volume. If our container expands or contracts, then work is being done, and we want to avoid that.

- When heat is equal to energy in a system performing no work, that heat is given a special name: enthalpy. The term "heat" might also pop up occasionally as a synonym in this special assumption that no work is done.

- When a chemical reaction takes place, enthalpy almost always changes hands in one way or another. It must either flow out of or into the reacting system. A reaction that releases heat to its surroundings is called an exothermic reaction. Conversely, a reaction that absorbs heat from its surroundings is called endothermic.

SPECIFIC HEATS AND HEAT CAPACITY

- If we devise a system that does no work, we can simply track how heat moves and use that to determine the total energy of a process. We measure heat by using temperature. But there is a catch. The temperatures of different substances change differently as they absorb or release certain amounts of heat.

- Metals, for example, tend to increase in temperature dramatically with the addition of just a small amount of heat. But other materials, most notably water, need much more energy to increase by the same temperature. These materials are said to have different specific heats. A specific heat for a substance is a measure of how much energy is required to heat 1 gram of material by 1° centigrade. This value is sometimes denoted in equations by S or c.

- Water has a specific heat of 4.18 joules per degree centigrade (J/g°C), which means that it requires 4.18 joules of energy to raise the temperature of 1 gram of water by 1 centigrade. In contrast, metals like copper have much lower specific heats—in many cases 10 times less than that of water.

- Specific heat is an intensive property, which means that it does not change with amount. The specific heat of water is 4.18 J/g°C no matter how much or how little water you have. But in practical situations, we don't always work with just 1 gram of water.

- So, we need a second parameter that is extensive, or dependent, on amount. This parameter is called heat capacity, denoted by C. Heat capacity is easily calculated if you know the mass of the sample you will be heating. We simply multiply the specific heat by the mass of the material, and we get a value with units of joules per degree centigrade. This allows us to directly correlate temperature change of an object to the heat transfer that caused that temperature change.

CALORIMETRY

- How do chemists actually measure the heat of a reaction? To get the answer to this question, we have to go back to the mid-1800s. French chemist Pierre-Eugène-Marcellin Berthelot was a contemporary of Joule, and just like Joule, the industrial needs of his day had driven him to study the storage and release of chemical energy.

- Far from being interested in beer brewing, however, Berthelot's passion was something that should never be mixed with alcohol: explosives. In an age when manufacturing and construction were booming, someone had to produce the raw materials, and that meant mining, which meant the use of explosives.

- To that end, Berthelot sought to understand the exchange of energy during explosions. The more he understood this, the better he could make his products.

- The value in explosives is in their ability to release energy in the form of work, but determining an explosive formulation's potential could be accomplished more easily (and much less destructively) by measuring the heat it generated when that explosive was detonated in a system that actually prevented it from doing work.

- In the real world, that is much easier said than done. First, in this case, the "surroundings" are the entire universe, except for the small sample of explosive being detonated. How do you measure the temperature of the entire universe?

- Second, when bombs go off, the matter making up the explosives is thrown about and mixes with the material around it. This would be detrimental because the system and surroundings must remain unmixed if we are to determine how energy flows between them.

- But Berthelot solved both of these problems in one ingenious design. He fashioned a device consisting of 2 chambers. The inner chamber was made of thick walls and sealed tightly to contain the explosive reaction that would take place inside. This chamber was so thick that no expansion took place during the reaction. In other words, no work was done. The outer chamber was filled with water and insulated from the outside world so that no heat could get in or out.

- Essentially, Berthelot created a miniature universe in which the system—the interior chamber containing the reacting explosives did no work—and the surroundings—the water filling the outer chamber—could absorb essentially all of the energy of the reaction as heat. He named this device a calorimeter.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 166–187.
Cobb and Goldwhite, *Creations of Fire*, chap. 11.
Masterton and Hurley, *Chemistry*, 8.1–8.3.

QUESTIONS

1. Name a few devices in your home that are designed to produce heat while doing as little work as possible. Now consider a few devices in your home that are designed to do as much work as possible while generating a minimum of heat. Do any of those devices fully succeed at reaching this design goal?

2. Methanol has a heat of combustion of –725 kilojoules per mole. Water has a specific heat of 4.18 joules per degree centigrade. By how many degrees can a 10-kilogram sample of water be heated using 1 mole of methanol?

Answer
2) 17.3°C.

Hess’s Law and Heats of Formation

LECTURE 17

State functions are simply defined as properties that are identical for all systems of a particular kind, no matter what has happened to that system previously. Russian chemist Germain Hess was the first to realize that enthalpy is a state function, meaning that heat change for a complex process is equal to the sum of the heat changes of its individual steps. As you will learn in this lecture, Hess’s law allows us to use an inventory of all the bonds broken and formed in a process to estimate the enthalpy change. You will also learn a more accurate technique for estimating enthalpy changes using heats of formation.

HESS’S LAW

- Pierre-Eugène-Marcellin Berthelot’s calorimeter gives us a way to measure the energy that changes hands when a chemical reaction takes place. Over decades, many scientists have used this device to measure the heats exchanged when many reactions take place, obtaining a great deal of information about how energy flows when chemical bonds form and break.

- It took a lot of work and time to catalog the heats released or absorbed by various chemical processes. Wouldn’t it be great if there were some way that we could get some of that information without having to actually run the experiment?

- Each time the heat of combustion for a given material is measured, it is always found to be exactly the same—no matter if the reaction is run quickly or slowly, with large excesses of oxygen or just enough. It doesn’t matter where the material came from or how it was made. For a given material, at the end of the reaction, the same amount of heat always changes hands. This fact is a crucial observation, because it means that the route that a chemical reaction takes to its products doesn't alter the energy that those products contain.

- This observation led to a law postulated in 1840 by a Swiss-born Russian chemist and physician named Germain Hess. Hess, who conducted an experiment using a calorimeter, was one of the first to realize that the enthalpy of any given system is always the same, no matter how it is made or what went into making it. In short, enthalpy is a state function. He worked this feature of enthalpy into a rule now known as Hess's law.

- Hess's law states that the enthalpy change for a complex process is equal to the sum of the enthalpy changes of the smaller steps making it up, no matter what those smaller steps might be.

- Hess's law is important because it allows us to take a shortcut to predicting the enthalpy of a reaction by running that reaction in our minds, completely disassembling molecules into their constituent atoms, and then putting them all back together into the products that we want to form. As long as we know the enthalpy changes associated with the smaller steps of our imaginary process, our result should translate to a meaningful enthalpy change for the reaction in the real world.

- This process would never happen in nature. In reality, chemical reactions take complex pathways of stepwise bond breaking and forming as they progress, but thanks to Hess's discovery, we can take a shortcut. In our minds, we can take any route from the starting materials to the products in our reaction. We simply run an imaginary reaction, knowing that the enthalpies of the starting and ending points should be the same no matter how the process really happens.

- One method that exploits that fact uses our knowledge of the energy released or absorbed when typical chemical bonds form or break. These are called average bond enthalpies.

- We can calculate the enthalpy of a reaction using bond enthalpies and Hess's law. We can add enthalpy to the reaction by breaking all bonds and remove enthalpy by forming new bonds.

- Hess's law gives us a way to use bond enthalpies. We catalog enthalpies just by measuring approximately how much heat is released when a certain type of bond forms, on average.

- Let's start by thinking about carbon and how it bonds to other things. When a carbon atom and a hydrogen atom come together and form a chemical bond, 413 kilojoules of energy per molar bond (kJ/mol) is released. That means that it would take that much energy to break it and reverse the process.

- The higher the bond enthalpy is, the stronger the bond will be. So, carbon-carbon bonds are pretty tough—they're 348 kJ/mol. Those are the bonds that are holding together the sugars in the foods that we eat and many of the molecules in our body. Carbon-nitrogen bonds are a bit weaker and, therefore, a little bit more reactive.

- Continuing with the halogens, carbon-fluorine and carbon-chlorine bonds are fairly sturdy, which explains why they're used so often in refrigerants, which can escape into the atmosphere. We want to use something that's not too reactive.

- Bromine and iodine, however, have weak bonds, and combining these elements with carbon would be dangerous to the environment. Carbon and sulfur also bond with relatively low bond enthalpy, making carbon-sulfur bonds somewhat reactive.

- Multiple bonds release different amounts of energy. For example, it takes 348 kJ/mol, on average, to break a carbon-carbon single bond, while it takes 614 kJ/mol to break a carbon-carbon double bond and 839 kJ/mol to break a carbon-carbon triple bond.

- How does Hess's law give us a way to use these apparently disparate energies in a way that lets us calculate how much energy changes hands when a molecule converts from one type to another?

- Hess's law allows us to take a set of reactants, convert it into anything we want in our minds, then convert that into the final product in a 2-step process, and then combine the heats that we expect to determine the overall heat of the process.

- Average bond enthalpies are an estimate of the amount of heat released when a bond forms or heat absorbed when it is broken, determined by averaging out the observed enthalpy for a particular type of bond forming over a range of situations.

- But not all bonds between 2 particular atoms are created equally. For example, the energy required to break the oxygen-hydrogen bonds in water are actually not identical. Breaking the first bond requires slightly more energy input—about 499 kJ/mol—and breaking the second takes slightly less—about 428 kJ/mol. These numbers are close to one another, but they are different enough to possibly be important.

AVERAGE BOND ENTHALPIES

BOND	ΔH (kJ/mol)
C — I	240
Cl — Cl	242
C — S	259
Br — Br	259
C — Br	276
C — N	293
H — I	299
C — Cl	328
C — C	348
C — O	358
H — Br	366
H — N	391
C — H	413
H — Cl	431
H — H	436
H — O	463
C — F	485
O = O	495
H — F	567
C = C	614
C = N	615
C = O	799
C ≡ C	839
C ≡ N	891
N ≡ N	941

- Using average bond enthalpies is great when we only need an estimate for the energy released in a reaction, because there are relatively few combinations of 2 bonded atoms. This makes for a very manageable table of values to have to scan. But what about when we need more precise numbers? Sometimes we have to just use an enthalpy value specific to the compounds we are studying.

HEATS OF FORMATION

- But what value should we use? We need something easy to compare from molecule to molecule. But what process should we use?

- Absolute enthalpies are actually impossible to know. We have to compare the enthalpy of a product to that of a set of starting materials if we are going to determine the change.

- But those starting materials can be anything we can imagine, so how do we choose? Why not choose something simple that we can all remember and agree on. How about pure elements in their standard states? That seems like the most logical place to start.

- This is exactly what chemists do. They arbitrarily define the enthalpy of any given element in its standard state as 0. The heat gained or lost when the compound of interest forms from elements in their standard states is measured, and this value is called the heat of formation for that compound.

- The heats of formation for H_2 gas, O_2 gas, and carbon as graphite are all 0 kJ/mol. But while diamond and ozone are pure carbon and oxygen, respectively, they are not in their standard state; ozone and diamond aren't the most stable form of these elements at standard temperatures and pressures.

- So, diamond actually has a nonzero heat of formation. Simply rearranging the atoms in graphite to form diamond requires the input of a small amount of heat—about 1.9 kJ/mol of carbon. And turning diatomic oxygen into ozone requires the input of 143 kJ/mol of heat, so ozone is clearly much less stable than diatomic oxygen.

- Now that we can spot elements in their standard state and realize that their enthalpies are 0, we can measure the heat change when any compound we can imagine is formed from its constituent elements in their standard states and assign that value as its heat of formation.

- We can estimate the heat of reaction on the combustion of propane instead of using bond enthalpies by using heats of formation, using the following equation: $\Delta H_{\text{reaction}} = \Delta H_{\text{f products}} - \Delta H_{\text{f reactants}}$, where ΔH is the change in enthalpy (heat) and *f* stands for "formation." The heat of formation of the products is positive, and the heat of formation of the reactants is negative.

- Heats of formation for various compounds give us a way to even more accurately estimate exactly how much energy changes hands in a variety of reactions. And it all hinges on the ideas of Germain Hess, published more than 170 years ago.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 187–196.
Masterton and Hurley, *Chemistry*, 8.4–8.5.

QUESTIONS

1 How does Hess's law allow us to use heats of combustion for food items to approximate the caloric content released during the complex biological process of metabolizing their nutrients?

2 Use the heats of formation for glucose, carbon dioxide, and liquid water (given below) to calculate the heat of combustion for 1 mole of glucose ($C_6H_{12}O_6$).

$$C_6H_{12}O_{6\ (s)} + 6O_{2\ (g)} \rightarrow 6CO_{2\ (g)} + 6H_2O_{\ (l)}$$

ΔH_f glucose = –1271 kilojoules per mole

ΔH_f $CO_{2\ (g)}$ = –393.5 kilojoules per mole

ΔH_f $H_2O_{\ (g)}$ = –285.8 kilojoules per mole

Answer

2) $\Delta H_{rxn} = 6(\Delta H_f\ CO_2) + 6(\Delta H_f\ H_2O) - \Delta H_f$ glucose = –2805 kilojoules per mole.

Entropy: The Role of Randomness

LECTURE 18

Chaos, randomness, and disorder might not be the first things that enter your mind when you think of the carefully controlled laboratory experiments of a researcher. Yet randomness seems to be all around us, ever creeping into systems of higher order. Rigid mountains chemically weather, becoming dissolved minerals, dispersed across rivers and oceans. Plumes of water vapor from smokestacks diffuse into the surrounding atmosphere without a trace. Materials just seem to naturally want to spread out. In this lecture, you will learn about disorder in the form of entropy.

ENTROPY

- To determine how heat flows during chemical changes, early physical chemists like Joule and Berthelot focused on simple systems in which no work was done. This allowed them to begin to crack the code of how energy flows during bond formation and breaking, by measuring heats of reactions in calorimeters.

- The early focus on heats of reaction led to an overemphasis on its importance in determining whether a chemical reaction is expected to happen. It was a widely held belief among chemists that for a reaction to happen, it must be exothermic, or heat-emitting.

- But there are many processes that defy this rule. For example, rapidly expanding gases actually get colder. Clearly, systems had a tendency to change in ways that release heat, but it is equally clear that there were many exceptions to this rule. All of these exceptions pointed to a second force pushing chemical reactions forward—a force so powerful that it could sometimes trump the influence of heat. But what was it?

- The answer to this burning question begins with an Austrian-born physicist named Ludwig Boltzmann. In the 1870s, as a young professor of mathematics, Boltzmann began to formulate a theory that would ultimately prove to be the final piece of the thermodynamic puzzle that explains why and how chemical systems change.

- He accomplished this not by focusing on heat, but on disorder. He stopped to consider just how disordered a particular system is and wondered if somehow a mathematical quantity could be assigned to indicate its level of disorder.

- We know from experience that matter behaves in very predictable ways. The gas in a balloon will always fill the balloon completely. Liquid water will always take the shape of the container that it occupies. A block of iron will retain its shape indefinitely.

- At a glance, it seems like the air, water, and iron are unchanging—in exactly the same configuration from one time to the next. If you inspect it at one moment, and then another, they appear to be the same. These states are called macrostates. They are a description of the material at the scale that we commonly encounter and understand them.

- But the macro scale wasn't the focus of Boltzmann's ideas. Boltzmann was concerned with the predictability of a system at the molecular and atomic level—what we call the micro scale.

- Samples of air, water, and iron contain billions upon billions upon billions of atoms and molecules, each of which can move, rotate, and vibrate. So, there are a huge number of potential positions and velocities for each atom and molecule in these objects at any instant in time.

- If we had a molecular camera that could photograph these objects at that level, taking pictures of them at different times, we would see atoms and molecules in differing positions, moving and vibrating in different ways each time.

- Boltzmann called these states—those that consider the position and motion of every atom in a system—microstates. And there are sometimes many microstates that can accurately describe any one macrostate.

- The macrostate of any collection of atoms or molecules can be consistent with any one of a number of microstates. Boltzmann formulated a famous equation that relates the randomness of a chemical system to the number of microstates accessible to that system. And the number of microstates can be genuinely staggering.

- Boltzmann's equation states that the randomness, or entropy, usually designated as S, is equal to Boltzmann's constant, k_B, times the natural log of the number of accessible microstates, W: $S = k_B \ln W$.

- This allows us to either take the number of microstates and from that calculate entropy or, more interestingly sometimes, determine from the measured entropy of the system exactly how many microstates it has accessible to it.

- Boltzmann's entropy calculation allows us to determine just how disordered a system is, based on how many microstates it can adopt. Combine this with nature's clear preference for disorder and you have a way of determining how systems, left to themselves, will change through time.

- Of course, they will trend toward disorder, because there are simply more microstates consistent with that macrostate. Left unattended, a house of cards is destined to become a disordered array of cards on the floor. An ordered wall is destined to become a disordered pile of bricks. Even ordered mountain ranges, some of nature's mightiest creations, are destined to become disordered beds of sand on a river delta over millions of years.

THE SECOND LAW OF THERMODYNAMICS

- The second law of thermodynamics can be stated any number of ways, but it essentially states that entropy, or randomness, in a closed system tends to increase unless it is countered by the input of energy from an outside source. Put even more simply, the universe is always becoming more random.

- Just like a house of cards, a wall, or even a mountain, if left to reach its own lowest energy state, a house will eventually crumble into a disordered pile of rubble. How do we prevent this change? Significant energy must be put in by the homeowner to keep this system in its desired macrostate. This is because there are many more microstates consistent with an unattractive pile of rubble than there are with a beautiful home.

- This is particularly disconcerting from a cosmological perspective, because cosmologists often think about the entire universe as one gigantic closed system. If we think in this way, Boltzmann's equation and the second law of thermodynamics make a dire prediction—that the overall randomness of matter in the universe will constantly increase until it simply can't any more. Because in theory there is nothing outside of the universe to act as a source of energy input, we are doomed by the second law of thermodynamics.

- This manner of thinking leads to the prediction that someday the universe will become completely randomized. A slave to the second law of thermodynamics, the entropy of the universe will continue to grow until the whole of the universe is a single uniform temperature. At this point, there will be no available energy left to power life, planetary processes, or even the vast engines of stars.

- Cosmologists call this phenomenon heat death, and if it is our destiny, then the only consolation is that it will take the universe billions upon billions of years to get there.

- Boltzmann's method of modelling entropy with microstates has ultimately proven to be correct. During his day, atomic theory, upon which his equation hinged, was still being hotly debated. It would take a few more decades and the support of one of the most revered physicists of his own day, Max Planck, to finally make Boltzmann's ideas stick.

- Nonetheless, Boltzmann is popularly given the credit for recognizing the connection between entropy and microstates. It is also worth mentioning that although Boltzmann gets the lion's share of the credit for this concept, it did have other advocates, including Lord Kelvin, whose famous temperature scale is validated by Boltzmann's equation. As happens so often in science, in this case, individual accolade fails to capture the spirit of community that truly brought about this revolutionary concept of entropy.

PREDICTING ENTROPY CHANGES IN CHEMICAL SYSTEMS

- Boltzmann's ideas about what we now call statistical thermodynamics were spot on. Nature gravitates toward randomness. Another clever way of stating this concept is that nature abhors a vacuum. In short, solids would rather be liquids and liquids would rather be gases, because each has a consistently increasing degree of disorder, or entropy.

- We can use this general rule to our advantage to help us predict when certain reactions will take place by considering how entropy changes as the system converts from its initial to its final state.

- A pure substance as a gas has greater entropy than one does as a liquid. And, by extension, a liquid in turn has greater entropy than a solid. This is because molecules in a liquid at least have free run of the volume the liquid contains. In a solid, by contrast, molecules are stuck in a fixed location, able only to shift and vibrate but not to move freely within the volume of the solid.

- The same general hierarchy of entropies applies to chemical reactions. When we want to analyze how entropy drives chemical reactions, first we have to look for gas formation or consumption, because atoms and molecules in the gas phase drastically increase the number of accessible microstates for a system.

- If the number of moles of gas increases as a reaction takes place, then the entropy of the system increases. In other words, ΔS is positive. Alternatively, if the overall amount of gas in the system decreases as the reaction progresses, then the entropy of the system is decreasing, and ΔS is negative.

CALCULATING ENTROPY CHANGES IN CHEMICAL SYSTEMS

- Just as with enthalpies, sometimes we need more than a hunch about the overall sign of entropy change associated with a system. We need an exact numerical value for the entropy change.

- Just like enthalpy, entropy is a state function. But unlike enthalpy, entropy is absolute. So, we can use a table of standard molar entropies, which can be found online, to obtain the experimentally determined molar enthalpy for any material we choose. The standard molar entropy of a particular compound will always be the same, no matter how it was formed or what conditions it has experienced before. Just as this allows us to determine standard enthalpy changes for reactions from tabulated data, it allows us to do the same for entropies.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 808–822.
Cobb and Goldwhite, *Creations of Fire*, pp. 225–226.
Masterton and Hurley, *Chemistry*, 17.1–17.2.
Stein and Powers, *The Energy Problem*, chap. 3.

QUESTIONS

1. Even if a mixture of gases appears to be perfectly uniform at the macroscopic level, is it ever perfectly uniform at the atomic or molecular level? If so, how rare is this condition of perfect uniformity at the molecular level?

2. Why is entropy reported as an absolute value, while enthalpy is always reported as a change relative to a reference point of pure elements in their standard state?

Influence of Free Energy

LECTURE 19

If the natural tendency of systems to lower their overall heat—or decrease their enthalpy, as Joule observed—and the tendency of a system's entropy to increase—as mandated by Boltzmann—ever collided, who wins? What happens when exothermic reactions reduce the entropy of a system? And what happens when endothermic reactions increase the entropy of a system? In this lecture, you will explore these questions as you learn about an equation that can account for both of these reaction-driving forces simultaneously, predicting which reactions we can expect to take place and which we can expect not to.

SPONTANEITY

› In common language, the term "spontaneity" invokes thoughts of something starting or happening quickly. But when chemists use this term, they aren't referring to speed. A spontaneous chemical reaction is simply one that will proceed to at least some extent without external assistance.

› Consider the combustion of hydrogen gas with oxygen gas to form water vapor. We know that this reaction releases a tremendous amount of heat. But the balanced equation—$2\ H_2 + 1\ O_2 \rightarrow 2H_2O$—shows us that the reaction is entropically disfavored. The equation tells us that 3 moles of gas starting materials produce just 2 moles of gaseous product. If entropy has its way, this reaction will not proceed at fixed temperature and pressure, but we know that it does.

- If you mix some hydrogen with some oxygen and use a spark to initiate the reaction, you will see a clearly spontaneous formation of water vapor, complete with the release of heat that we are accustomed to observing when a fuel like this is burned. In this case, energy is given off as heat as the reaction progresses without outside assistance.

- Entropy loses this battle. The reaction releases so much heat that the decreased randomness within the system is overcome. Enthalpy wins.

- When we dissolve a solid salt called ammonium nitrate in distilled water, there is a drastic and precipitous drop in temperature. This endothermic process happens because what was solid ammonium nitrate dissolves into solution, where it's in a liquid phase. This means that entropically, the process of dissolution is favorable, but from an enthalpic standpoint, it's not, because it's absorbing a tremendous amount of heat.

- Let's consider an endothermic chemical process, as opposed to the physical process of dissolving the ammonium nitrate. We start by sprinkling a little water onto a wooden board, and then we run a reaction between 2 solids—barium hydroxide and ammonium thiocyanate—in a beaker placed on that board.

- First, we add ammonium thiocyanate to the beaker, and then we add barium hydroxide to the beaker. Because those reagents are in the solid phase, we have to stir them to get them in contact and give them a chance to react. After some time, the mixture starts to become a bit slushy—almost as though some kind of liquid is forming.

- We went from 2 solids to a product that contains liquid, which means that this process is quite favorable entropically. The outside of the beaker becomes very cold—so cold, in fact, that the beaker becomes frozen to the board. Entropy wins the battle, and this reaction proceeds even though it is endothermic.

- In this case, the heat, or enthalpy, of the system increased, but dissolution increases the randomness, or entropy, of the system. This process and others like it are used in portable cold packs carried by athletic trainers and emergency medical technicians.

GIBBS FREE ENERGY

- There are not only plenty of processes for which enthalpy and entropy are working against one another, but there is no guaranteed winner when they are opposed. But so far, our thought experiments haven't been able to tell us which reactions will be spontaneous and which will not. For that, we need to invoke the work of J. Willard Gibbs, an American-born scientist and a contemporary of both Joule and Boltzmann.

- Throughout the late 1800s, Gibbs made numerous contributions to the science of thermodynamics. Arguably none of his offerings was greater than his equation for what has come to be known as the Gibbs free energy change for a process. The Gibbs free energy gives us a way to combine enthalpy and entropy mathematically to determine whether the standard molar energy change for a process is positive or negative.

- Just as before with enthalpy and entropy, we will be concerning ourselves with standard free energy changes, meaning that these energies are determined at 298 Kelvins, or about 77° Fahrenheit, and 1 atmosphere of pressure. These values can vary with conditions, but ΔG is a very good indication of the overall behavior of processes near standard conditions.

- A positive free energy change means that the reaction absorbs energy overall, so it is not going to take place without some outside assistance in the form of energy input. Therefore, we would call a reaction like this non-spontaneous. But a negative energy change means that the reaction releases energy to its surroundings and will happen all on its own, making it spontaneous.

- The Gibbs free energy equation is $\Delta G = \Delta H - (T)\Delta S$, where ΔG is the free energy change, ΔH is the enthalpy change, T is the absolute temperature, and ΔS is the entropy change. This equation includes a term for enthalpy and a term for entropy, unifying these 2 forces and helping us divine which one wins in a conflict, or exactly how much each one participates in defining the spontaneity of a reaction.

- According to this equation, entropy's contribution to the spontaneity of a reaction is modified by the temperature—it is temperature dependent—whereas enthalpy change is not, which means that temperature will have a profound effect on whether the reaction will take place.

- But we can go even further than simply predicting if a reaction will be spontaneous always, never, or at higher or lower temperatures. We can take Gibbs's equation to the extreme and actually determine the magnitude of the standard molar free energy change for a compound. All that we need are the standard molar enthalpy and standard molar entropy of the reaction and the temperature at which it's run.

- Just as we can estimate things like enthalpies and entropies using our knowledge of chemistry, we can also get a rough estimate of how the free energy of a system will behave simply by knowing the signs of those changes.

- In the Gibbs free energy equation, temperature is absolute, so it's always positive. We have to use Kelvins in this equation as our temperature term, but ΔH and ΔS can both have varying signs, which leads to 4 possible permutations of ΔH and ΔS signs. From those 4 permutations, we can begin to tell how temperature will affect spontaneity and reactions.

- For example, let's say that we have a process in which ΔH is positive and ΔS is negative. In this case, ΔH is going to be working against spontaneity, because it's going to create a positive contribution to G. Entropy will be doing exactly the same thing. It's going to slow the reaction down—or, rather, it's going to decrease its spontaneity—because a negative entropy is being subtracted. In the case of a positive enthalpy and negative entropy change for process, that process can never be spontaneous at or near standard conditions.

- An example of this is the formation of diamond. We simply can't expect pencil lead to turn into diamond on a countertop.

- If, however, ΔH is positive but so is ΔS, that means that ΔS will be contributing to spontaneity. The effect of ΔS is amplified at higher absolute temperature, so in this case, we'll have a reaction that is more spontaneous at higher temperatures. Simply by increasing the temperature, we can anticipate that we'll make the reaction more spontaneous.

- An example of this is the melting of ice—a very familiar process that we know only happens when the temperature is sufficiently high.

- In situations where we have a negative enthalpy, the enthalpy is contributing to spontaneity. The more heat that is released, the more spontaneous a reaction will be, because that will create a more negative ΔG. If we have a positive entropy change going along with it, because entropy is subtracted, this means a greater term being subtracted and an even greater negative number. In other words, when the ΔH is negative and ΔS is positive, a reaction will always be spontaneous at or near standard temperatures and pressures.

- A good example of this is the combustion of propane. Propane and oxygen will always combine to spontaneously form carbon dioxide and water. It's a question of how long it will take, but never whether it will happen. Propane and oxygen are destined to become carbon dioxide and water.

- If we have a negative ΔH, which contributes to spontaneity, but a negative ΔS, which is working against us, to minimize the effect of entropy, we'd have to lower the temperature to make the reaction more likely to be spontaneous. In other words, it's spontaneous at low temperatures.

- An example of this reaction is the combustion of hydrogen. Combusting hydrogen and oxygen together creates only 2 moles of water vapor, which is entropically disfavored, so at lower temperatures, this reaction is more favored.

- Free energy combines the enthalpy and entropy considerations, giving us a unifying equation that can help explain why propane burns across a wide range of temperatures or why water boils at 100° centigrade. The impact of Gibbs's free energy equation is indisputable. It gives us a way to quickly and easily predict which reactions will be spontaneous and which will not over a range of conditions.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 822–835.
Cobb and Goldwhite, *Creations of Fire*, pp. 226–229.
Masterton and Hurley, *Chemistry*, 17.3–17.4.

QUESTION

1 The Haber process for nitrogen fixation is a chemical reaction that changed the course of human history on many levels. It uses hydrogen and nitrogen gases as reactants to form ammonia using the following reaction:

$$3\ H_2\ _{(g)} + N_2\ _{(g)} \rightarrow 2\ NH_3\ _{(g)}$$

ΔH°_{rxn} = –93 kilojoules per mole

ΔS°_{rxn} = –198 joules per mole Kelvin

Based on the standard enthalpy and entropy for the reaction, calculate the Gibbs free energy for the reaction at standard conditions. Is this reaction spontaneous under standard conditions?

Answer

1) $\Delta G = \Delta H - (T)\Delta S$ = –39 kilojoules per mole. This reaction is spontaneous under these conditions.

Intermolecular Forces

LECTURE 20

The focus of this lecture is on phase changes. The 3 common phases of matter are solids, liquids, and gases. In general, on the macroscopic level, solid matter is matter that has fixed volume and shape. Liquids have fixed volume but not fixed shape. Gases have neither fixed volume nor fixed shape, because they naturally expand to fill their container. In this lecture, you will consider these 3 phases of matter on the molecular level.

THE MOLECULAR PERSPECTIVE

› Chemistry explains the phases of matter by considering how strongly molecules, atoms, and ions of a particular substance attract one another. Attraction is a force, and the attraction one molecule has for another molecule of the same kind is called an intermolecular force.

› If the molecules in a sample of matter are attracted to one another very strongly, they will stick together with such tenacity that they lock one another into a fixed location within the sample. They cannot move independently. They cannot even move relative to one another. They form a rigid object that can't expand or even change shape.

› But what if that attractive force is just slightly weaker? In this case, the molecules might maintain contact with one another but be free enough to slide along one another, moving freely with the constraint that they never completely separate from the sample. So, they form an object that can alter its shape but can't expand or contract to change its volume.

› And what if those attractive forces were weaker still—so weak that the molecules in the sample can completely overcome them with kinetic energy, freeing themselves to move truly independently of all others in the sample? A sample like that could change not only its shape, but also its volume.

- We just characterized solids, liquids, and gases like a chemist does. It is all about the battle between kinetic energy and intermolecular forces.

- In the case of pure substances, we break down these forces into 3 subcategories: London dispersion forces, dipole-dipole interactions, and hydrogen bonds.

LONDON DISPERSION FORCES

- London dispersion forces are temporary attractive forces that form when, just for an instant, the electron cloud of an atom or molecule becomes imbalanced. This is most easily pictured using very small monoatomic elements like helium atoms.

- Helium has 2 electrons per atom, both of which are held in the 1*s* subshell. But these 2 electrons are free to move essentially independently of one another within that space, so naturally there is a likelihood that one might find both electrons on one side of the atom at any given time.

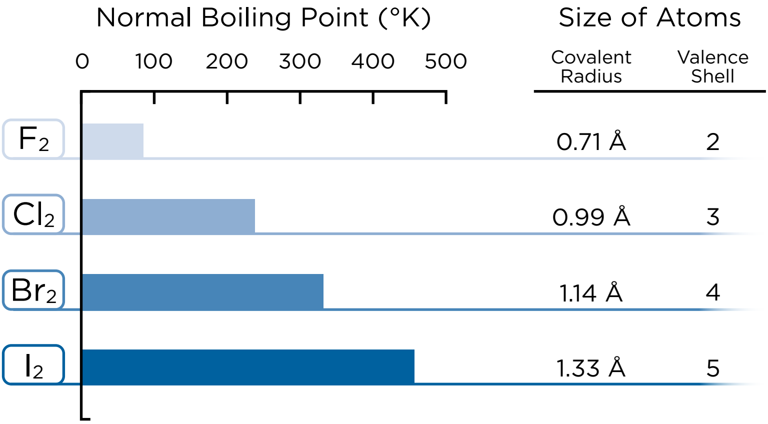
- When this happens, for a length of time not much longer than an instant, a charge separation can form in the atom, with the negative end pointing in the direction of the electrons and the positive end at the opposing side.

- But in that instant, another nearby helium atom can sense that dipole, and its electron cloud shifts to create a dipole that aligns itself in such a way that the 2 atoms slightly attract one another.

- In the case of helium, this effect is extremely tenuous because of how tightly the 1*s* electrons are held by the nucleus. But as atoms and molecules become larger and larger, and their electron clouds grow in size, interior electrons screen outer electrons from the nucleus, making them more susceptible to being pushed around from the outside of the atom. As a result, the intensity of this effect increases.

- The influence of dispersion forces can be observed in the boiling points of molecular halogens. Consider fluorine, chlorine, bromine, and iodine, all of which are halogens and form diatomic gases.

- There is a very pronounced trend in their boiling points, with iodine having the highest and fluorine having the lowest. We can analyze this trend if we think about the atomic radii of these elements. Fluorine has the smallest atomic radius, and iodine has the largest. They follow the same trend as the boiling points do.



- If we consider their valence energy shells, fluorine is a second-row element, chlorine a is a third-row element, and so on. Each of these has a progressively larger and larger shell of electrons, which is progressively screened more and more from the nucleus at the center.

- This means that it's easier to induce a momentary dipole in an iodine molecule than in a bromine molecule, and so on. This is a very clear indication of the potency of these dispersion forces, indicating the physical behavior of certain materials.

DIPOLE-DIPOLE INTERACTIONS

- The second intermolecular force is known as a dipole-dipole interaction.

- Water molecules have a permanent dipole, owing to their bent molecular geometry, but carbon dioxide's linear molecular geometry means that it does not have a molecular dipole.

- The effect of having a permanent molecular dipole is to create an even more powerful attraction between and among molecules in a pure sample. For the same reason that transient dipoles align to form London forces, permanent dipoles can also align to form attractive relationships between and among molecules in a sample.

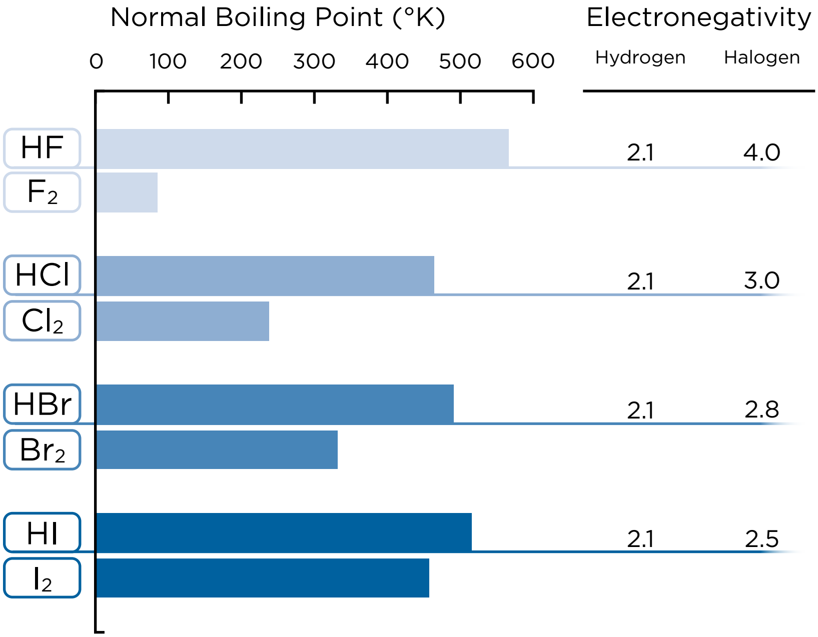
- The difference is that the charge separations in polar molecules are not only permanent, but also often stronger than those found in dispersion forces. As a result, we see that molecules of similar size tend to attract one another much more powerfully when they have a larger permanent molecular dipole.

- So, dispersion forces result from transient distortions in large electron clouds, and dipole-dipole interactions occur because of permanent charge separations across molecules due to a combination of polar bonds and their geometry.

HYDROGEN BONDS

- When we analyze the trends in boiling points of not only the molecular halogens chlorine, bromine, and iodine, but also the trends of what are called hydrohalides, we see a slight difference.

- Consider the fact that the hydrohalides HCl, HBr, and HI all have higher boiling points than their corresponding molecular halogens: Cl_2, Br_2, and I_2.



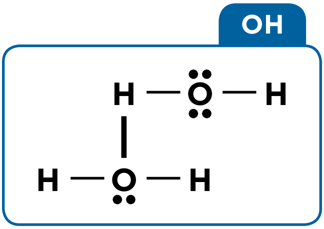
- Because a large, heavy iodine atom, for example, has been exchanged for a small hydrogen atom with a very small electron cloud that is close to the nucleus, the polarized ability of these hydrohalides is lower. Wouldn't they then have a correspondingly lower boiling point?

- The reason that they don't is because there is now a molecular dipole to consider, whereas the halogen molecules had 2 identical atoms bonded together and therefore no dipole.

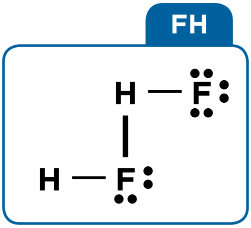
- These 3 compounds have very strong molecular dipoles, with chlorine forming the strongest dipole, followed by bromine and iodine. This explains not only the trend that we saw in terms of the hydrohalides having a higher boiling point, but also the fact that their boiling points don't drop off as precipitously as we moved from the right to left across the diagram.

- Hydrogen bonds, the third intermolecular force, are intermittent but powerful attractions that take place between a very positively charged hydrogen and lone pair electrons from an atom carrying a very strong negative charge. When this happens, 2 molecules can attract one another more strongly than one would simply predict from London forces and molecular dipole interactions.

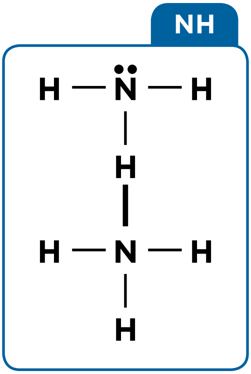
- The phenomenon of hydrogen bonding occurs when a very strong, dense dipole is present in a bond between hydrogen and a small nonmetal nucleus. Specifically, this effect only happens when an OH, NH, or FH bond is present.



- The hydrogen bond gives us a way to understand why water is a liquid at room temperature even when its chemical cousins are not. The molecular dipole of water is responsible for its remarkably high boiling and freezing points.



- It also lets us explain another fascinating property of water, one that is quite unusual: Solid water is less dense than liquid water.



- In a crystal of ice viewed at the molecular level, the hydrogen of one water molecule points toward a neighboring water's oxygen atom. That oxygen atom has 2 lone pairs and significant negative charge because of the polarity of the O-H bond.

- Because water is an AX_2E_2 molecule, that oxygen atom has 2 lone pairs of electrons that can interact with the hydrogen atom, forming an intermittent but strong interaction.

- To achieve this arrangement, the water molecules must align themselves in such a way that large gaps of empty space are left between them. This means that when compared to its liquid counterpart—in which water molecules are free to slip past one another, rotate, and pack as tightly as possible—solid water (ice) actually has less mass per unit of volume.

- At its freezing point, the density of ice is only about 90% that of liquid water. This is the reason that ice floats on liquid water.

- This is a critical property of water from an environmental standpoint, because each year large portions of the globe reach freezing. As it forms, buoyant ice rests on top of bodies of water, insulating and protecting the life and currents in the liquid below.

- If it weren't for hydrogen bonding, solid ice would instead fall to the bottom of bodies of water, leaving the surface exposed to the subfreezing temperatures of winter air. Entire lakes and possibly even oceans could easily freeze solid, wreaking havoc on those ecosystems.

- It is that same expansion—driven by hydrogen bonding—that is the reason behind the power of water to force boulders apart, driving geologic weathering processes, and to open gaping potholes in roadways, keeping your local tow shop in business.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 443–453.
Masterton and Hurley, *Chemistry*, 9.3.

QUESTIONS

1 Can it be said that dipole interactions are always stronger than dispersion forces? If not, offer an example of when this assumption is not true.

2 Methane (CH_4) boils at −161.5°C. Silane (SiH_4) boils at −112°C. How can intermolecular forces be used to explain this difference in behavior?

Answer

2) Although the Si-H bonds in silane are more polar than the bonds in methane, these bond dipoles cancel out, making both molecules nonpolar. Because silicon has a larger electron cloud than carbon, silane will have greater intermolecular dispersion forces, leading to its slightly higher boiling point.

Phase Changes in Matter

LECTURE 21

In this lecture, you will learn how the 3 most common phases of matter—solids, liquids, and gases—interconvert and consider the influence that temperature and pressure have on these transitions. You will also learn about phase diagrams, which are graphical tools used by chemists to predict the phase behavior of a pure substance based on the temperature and pressure conditions it is placed under. You will learn about some important features of these diagrams and some common phase transitions, as well as how heats of fusion can be used to predict how much energy will change hands as these transitions occur.

PHASE DIAGRAMS

- So far, we have thought only about how substances behave at or near what we call standard conditions: 25° centigrade and 1 atmosphere of pressure. Under these conditions, we know that certain materials (such as iron) are solids, others (such as water) are liquids, and yet others (such as nitrogen) are gases. But iron can be a liquid when it is molten. Water can exist in all 3 common phases, and gases like nitrogen can become liquids under the right conditions.

- The phases of materials can interconvert depending on conditions. When conditions are just right, solids, liquids, and gases can interconvert, going through some familiar and some not-so-familiar processes. Let's break down the effect of these 2 influential conditions: temperature and pressure.

- Chemists think of temperature as a measure of the kinetic energy of molecules and atoms. The higher the temperature of a material is, the more vigorously its constituent atoms or molecules vibrate, rotate, and move within the sample. The higher the temperature, the more kinetic energy those fundamental particles will contain, on average.

- In solids, molecules have precious little ability to move. They can only vibrate, but are held fast by the intermolecular forces that bind them to their neighbors. Because the molecules don't have sufficient kinetic energy to overcome those intermolecular forces, we expect a given material to be a solid at lower temperatures.

- When we raise the temperature somewhat, we are giving those molecules enough energy to slip past one another and move within the volume of the sample but not separate from one another completely. We create a liquid when we increase the kinetic energy of the molecules to a point at which their kinetic energy and intermolecular attractions are somewhat in balance.

- When we raise the temperature yet again, we give the material enough kinetic energy to completely overwhelm the attractive intermolecular forces. We change the liquid to a gas.

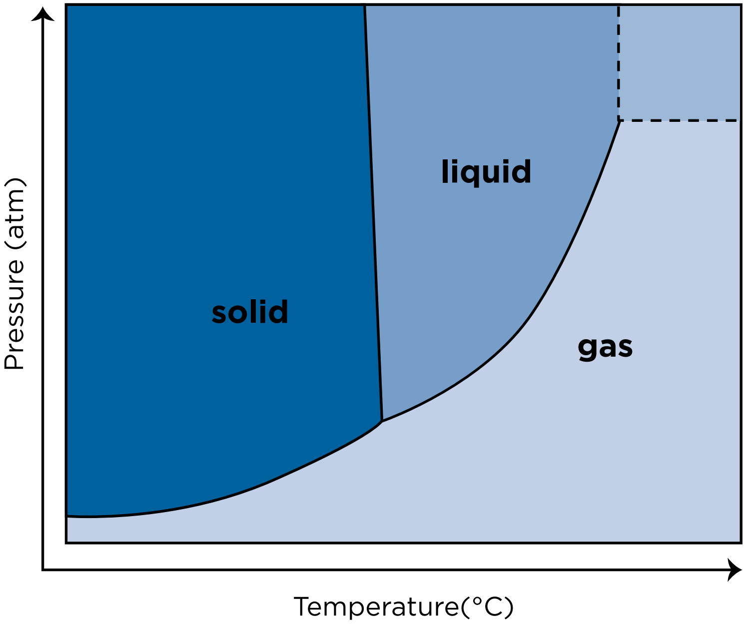
- Heating materials causes them to change from solids to liquids and again from liquids to solids. This trend holds for all but the most unusual and exotic materials.

- The second parameter, pressure, is simply a measure of how hard the atmosphere pushes in on a substance from all sides. Squeezing things makes them want to adopt a state that increases their density. On the molecular level, molecules and atoms can increase the density of a material by glomming together into a liquid or solid, whereas taking on a gaseous phase leads to much less dense material.

- Applying pressure to a substance encourages it to become a liquid or solid, while reducing pressure makes it more likely to take on the form of a gas.

- When chemists compile a catalog of material phases under different conditions of pressure and temperature, they can create what is known as a phase diagram. A phase diagram gives us a way to illustrate and demonstrate how and why a pure substance will change phases.

PHASE DIAGRAM OF H_2O



- How do we expect pressure and temperature to affect the phase behavior of a pure substance? When things get cold, they tend to solidify, and when they solidify, they tend to become more closely packed as molecules, which means that we expect the increase of pressure and decrease of temperature to create solids. Alternatively, we expect that if we increase the temperature of a substance, we would get a gas at low pressure. Liquids will usually fall somewhere in between solids and gases.

- A phase diagram gives us the exact condition boundaries between and among these 3 phases. It tells us exactly when and how these phases will interchange. The conditions that are favorable for a solid form a field in the phase diagram. Similarly, so do liquids and gases.

- In a phase diagram, there is only one unique set of conditions at which the solid, liquid, and gas can all coexist at equilibrium. This special point is called the triple point.

- Another important point is called the critical point. This is the set of temperature and pressure conditions at which liquids and gases become essentially indistinguishable from one another, creating a new phase of matter called a supercritical fluid.

- As we cross the boundary between solid and liquid, the substance would be melting and freezing, depending on the direction we're moving. Similarly, if we were to cross the boundary between liquid and gas, we would be describing boiling or condensation, depending on the direction.

- There is a third boundary between solids and gases at lower pressures. These 2 phases can also directly interchange in processes that we call sublimation, when we go from solid to gas, or deposition, when we go from gas to solid. The phase diagram gives us a way to determine at exactly what temperature and pressure conditions we expect all of these changes to take place.

- Processes like sublimation and phases like supercritical fluids may seem unfamiliar and exotic, but they aren't so unusual.

- The process of freeze-drying, used to preserve food, is accomplished by freezing food down to the temperature of liquid nitrogen and then placing it under a powerful vacuum to reduce the pressure to about 1⁄1000th that of Earth's atmosphere.

- Under these conditions, the water in the food converts from solid ice directly into water vapor through sublimation, because the pressure is below that of the triple point. This process not only allows for the dehydration of materials like coffee and ice cream, but also results in extremely dry products—so dry that virtually all water is removed.

- The reverse process, deposition, is commonly used to create extremely thin coatings for machined tools. Using a process called chemical vapor deposition, a vapor of carbon is deposited onto metal under precise conditions to create diamond-coated saw blades that offer the toughness of diamond without the price tag to go with it.

- Supercritical fluids are also more commonplace than you might think. Supercritical carbon dioxide can be created at about 50 atmospheres of pressure and has remarkable solvent properties. It can be used to clean garments or medical equipment and even finds use in decaffeinating coffee. Possibly the best part about it is that at the end of the process, the pressure can be reduced and the solvent becomes a gas, which simply escapes into the atmosphere.

HEATS OF FUSION

- Every material in any given phase has a specific heat, which allows us to determine the amount of energy needed to raise the temperature of that substance by a given amount without changing its phase. When we start and finish with the same phase, it is a pretty simple exercise to understand where all of that energy goes.

- But what happens when we heat or cool an object to such an extent that the phase changes? The flow of energy and its effects on the molecules within the sample can be a bit more complicated.

- The key to inducing phase change is to give or take away enough energy for the molecules comprising a substance to either overcome or succumb to the intermolecular forces trying to hold them together. This process of overcoming intermolecular forces actually requires energy itself, so during a phase change, there is no change in the temperature of a sample.

- As a sample of ice warms to 0°, there is no liquid water at all. The molecules of the solid are simply increasing in kinetic energy, causing the temperature of the sample to increase.

- But at 0° centigrade, as the phase change begins, the temperature holds steady at 0° throughout the entire transition. This is because the thermal energy coming into the sample from the heat source is now going into overcoming the forces that are holding the water molecules locked in place, rather than increasing its temperature.

- Because the energy being added is going toward promoting the process of melting, that energy does not increase the temperature of the sample.

- Once the conversion is complete, we can continue heating the liquid sample, increasing its temperature until another phase change begins—that of boiling. The temperature stabilizes as the energy input goes toward altering the phase of the sample rather than its temperature.

- During this time, steam is escaping from the sample, but if we contained the steam and continued heating it, we could increase its temperature even more, but only after the phase transition of boiling were complete.

- Just as there is a known specific heat for each phase of water, there is also a known heat required to melt or boil any given substance. In the case of melting, this is called the heat of fusion. When discussing boiling, we use a term called the heat of vaporization. Just like chemical reactions, these physical phase changes can go either way, so the amount of heat absorbed by water on melting is exactly the same as that absorbed on freezing.

- These values can be used to track heat as a sample undergoes transition processes. But how do we calculate the exact amount of energy that transpires during the transition process for a particular substance? Hess's law tells us that if we calculate the energy change in all of the transitions that a substance goes through, we can add them up and determine exactly how much heat must have moved.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 455–459, 462–464.
Masterton and Hurley, *Chemistry*, 9.1–9.2.
Seaburg and Paterson, *The Ice King*.

QUESTIONS

1 The heat of vaporization for water is much larger than its heat of fusion. This is true for most materials. Why are heats of vaporization typically so much larger than heats of fusion?

2 How much heat is required to convert 1 gram of water at 80°C to steam at 150°C?

Answer
2) 3156 joules.

Behavior of Gases: Gas Laws

LECTURE 22

As you will learn in this lecture, even though gases are tremendously versatile materials, there are only a few time-tested rules that can be generally applied to all gases. Collectively, these rules are called gas laws, and understanding them is critical to appreciating what a remarkably versatile yet predictable medium gases can be. The main properties of gases that can change in different situations include pressure, volume, temperature, and amount. As disparate as these properties might seem, they are all very closely related to one another, and their relationships constitute some of the most fundamental laws and theories of chemistry.

BOYLE'S LAW

- The long road to a law unifying the basic properties of gases begins in the 17th century with the Anglo-Irish philosopher, theologian, and chemist Robert Boyle. Although he was a productive publisher in the fields of philosophy and theology, Boyle's greatest contributions to Western thought were almost certainly his work in the fledgling field of chemistry.

- Mathematically, Boyle's law, most simply stated, is that pressure is proportional to the reciprocal of volume: $P = 1/V$. What that means is that if we have 2 identical samples of gas and we apply pressure to one of them, increasing the pressure on it, we expect the volume to decrease a proportional amount. If we double the pressure, we must therefore halve the volume, all other things considered equal.

- Starting with the obvious equality $P_2V_2 = P_2V_2$, Boyle's law allows us to create $P_1V_1 = P_2V_2$ through some substitutions. In other words, for any ideal gas, all other things considered equal—including number of moles, temperature, etc.—the pressure times the volume must be equal to a constant.

- So, Boyle demonstrated that at fixed temperature, the pressure of a gas sample is inversely proportional to the volume that it occupies. This mathematical relationship is the first key to understanding the behavior of gases.

GAY-LUSSAC'S LAW

- But there is more to our quest to formulate a comprehensive description of how gases behave. The next piece of the puzzle begins with French physicist Guillaume Amontons, who was the first to make a comparison between the temperature and pressure of gaseous systems.

- Amontons was working in the early 1600s and without the type of precise instrumentation that would be necessary to fully nail down the relationship between these 2 properties. What he did realize, however, was that when a sample of gas in a fixed volume was cooled from the boiling point of water to the freezing point of water, the pressure always decreased by about ⅓.

- Unfortunately for Amontons, lack of appropriate instrumentation made testing his theories difficult in his day. It would take another century until another Frenchman, Joseph-Louis Gay-Lussac, would publish measurements reliable enough to establish a scientific law. So, the fame largely goes to Gay-Lussac, although the term "Amontons's law" might also be used to describe this relationship.

- Gay-Lussac's law tells us that pressure and temperature must be proportional when all other things are held constant: $P = T$. In other words, if we were to increase the temperature of a sample by a factor of 2, we expect the pressure of it to increase by a factor of 2.

- Mathematically, we can create a substitution into this simple equality, $P = T$, that allows us to get a relationship between the pressure and temperature of any 2 ideal gases that we choose: $P_1/T_1 = P_2/T_2$. This is a very common way to represent Gay-Lussac's law.

- If you live in an area with seasonal climates, you have almost certainly noticed that your car tires always seem to need a little bit of air put in them when the winter months come. This is Gay-Lussac's law in action. As the ambient temperature drops, the pressure of the gas contained in your tires drops, causing that light on the dashboard to activate on the coldest days of the year, even when your tire has no leak.

CHARLES'S LAW

- The third relationship is between temperature and volume. We already know from the work of Amontons and Gay-Lussac that heating gases at a constant volume increases the pressure that they exert, but what if we interchange the roles of pressure and volume? What if instead we heat or cool a sample of gas under constant pressure?

- The answer to this question came from the work of Jacques Charles, yet another French investigator from the 18th century and also one of the West's first balloonists. Charles was heating gases and observing them just like Amonton and Gay-Lussac, but the key difference is that his system—a balloon—did not maintain a fixed volume. The walls of his balloons could expand, changing their volume in response to temperature.

- Charles famously tested a number of gases as potential fillers for hot-air balloons, and he noticed that regardless of which gas he used, his test balloons always expanded by the same amount when heated to the same extent. This remarkable result became the inspiration for Charles' s law, which states that when pressure is held constant, a sample of gas will increase in volume proportionally to its absolute temperature: $T = V$.

- If we double the temperature of a gas sample, using absolute temperature units like kelvins, Charles's law tells us that the new volume will be 2 times that of the original volume. Starting with yet another simple equality, we can arrive at an equation that allows us to relate the temperature and volume of any sample when all other things are held constant: $T_1/V_1 = T_2/V_2$.

- Charles's law has clear applications in aviation, explaining and predicting how heating the air inside of a balloon causes it to expand and become buoyant in the atmosphere. But it can also help us solve everyday problems.

- According to Charles's law, if you were to cause a gas to expand under constant conditions, the temperature of that gas should proportionally drop, causing a release of heat. If we were to compress that vapor again somewhat, the temperature of the sample should rise, absorbing heat.

- Charles's law explains how modern refrigeration systems work. A refrigerant absorbs heat in the cooling compartment and then releases it in a separate region of the device. But modern refrigerators, sometimes called vapor-compression systems, don't rely on the heat of vaporization, but rather keep the refrigerant in the gas phase, simply compressing and decompressing gas as it flows into and out of the cooling region of the refrigerator.

AVOGADRO'S LAW

- Amedeo Avogadro, the Italian chemist whose name is attached to the mole, is also known for a famous law, which he published in 1811, shortly after Gay-Lussac's law had gained acceptance. Avogadro noticed that at fixed conditions of volume, temperature, and pressure, samples of gases always seemed to have a mass that was proportional to the molecular or atomic mass of the gas.

- Essentially, Avogadro's law states that under constant conditions of pressure and temperature, an equal volume of gas contains an equal number of particles. From this, we can infer a more useful relationship that is more commonly presented as Avogadro's law now: the proportionality of the number of atoms or molecules to the volume that they occupy.

- The simplest way to state Avogadro's law mathematically is that the volume of a sample is proportional to the number of moles in that sample, all other things considered equal (pressure and temperature): $V = n$.

- In other words, if we have 2 identical samples and we double the number of moles in one of the samples, to maintain constant pressure, that volume will expand by a factor of 2: $n_2 = 2n_1$ and $V_2 = 2V_1$. Using Avogadro's observations, we can make some substitutions to get a more useful equality that isn't quite so obvious: $n_1/V_1 = n_2/V_2$. Under conditions of constant pressure and temperature, Avogadro's law gives us this ratio, or proportionality, for any ideal gas.

- Avogadro's law is the principle that underpins technologies like pneumatic pistons. A typical pneumatic piston design relies on the introduction of gas from a pressurized container into a sealed compartment within the piston. As the number of gas molecules inside the piston increases, its volume must also increase. It is this expansion that the piston turns into motion, tapping the process to create usable energy.

COMBINED GAS LAW

- Natural systems are complex and often undergo changes in temperature, volume, pressure, and quantity all in a single process. If each of these relationships is independently true, then we should be able to combine them into a single equation that will describe how they might all change in concert as a more complex process takes place.

- The combined gas law is the first of the gas laws to exploit some similarities among all of the other gas laws—specifically, Boyle's law, Charles's law, and Gay-Lussac's law. Boyle's law is that pressure is proportional to 1 over volume: $P = 1/V$. Charles's law states that volume is proportional to temperature: $V = T$. Gay-Lussac tells us that pressure is proportional to temperature: $P = T$. We can combine them to get an equation, called the combined gas law, that shows that pressure, volume, and temperature are all interrelated, and changing any one, or even all 3, of them should have effects that we can predict:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}.$$

IDEAL GAS LAW

- The combined gas law gives us a useful tool to predict how closed systems will react to changes in pressure, temperature, and volume. But where does Avogadro's law fit in? Based on our expression of Avogadro's law, which is $n = V$, we can insert it into the combined gas law and complete our unified equation to describe the behavior of gases:

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}.$$

- This is essentially the ideal gas law, but we're used to seeing it written a little differently. If $(P_1V_1)/(n_1T_1)$ always equals $(P_2V_2)/(n_2T_2)$, then those terms must be constant. That constant value is R, the ideal gas constant. Both of these pieces are equal to the same value, R:

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} = R.$$

If that's true, then we can rearrange these equations for any gas as $PV = nRT$, a much more common version of the ideal gas law, all based on the same mathematics and relationships as the previous version.

- The ideal gas law is the king of all the gas laws. This equation, which took a century to construct, allows us to predict any of the 4 variables that it contains under any conditions we want.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 399–416.
Cobb and Goldwhite, *Creations of Fire*, 202–210.
Masterton and Hurley, *Chemistry*, 5.1–5.2.

QUESTIONS

1. The gas laws discussed in this lecture depend on the assumption that gases behave ideally (their particles have negligible volume and completely elastic collisions with one another). What characteristics should a gas particle (atom or molecule) have to behave most ideally? Based on the answer to this question, which noble gas is expected to behave most ideally?

2. Predict the effects of the following changes on 1 mole of an ideal gas:

   a. Heating it from 100 kelvin to 200 kelvin at constant pressure

   b. Compressing it from 2 liters to 1 liter at constant temperature

   c. Allowing exactly ½ of the gas molecules to escape a container of constant volume

Answers

2a) The volume will be doubled; 2b) The pressure will be doubled; 2c) The pressure will be reduced by half.

Kinetic Molecular Theory

LECTURE 23

This lecture is about kinetic molecular theory. You will explore the kinetic energy of gaseous materials and how the molecules that comprise them each act like very small moving bodies in physics. You will also consider how to treat a gas sample as a whole, which is a huge collection of independently moving particles. In addition, you will learn that both average energy and rms velocity are dependent on the temperature of the sample and the molar mass of the gas particles. Furthermore, you will be introduced to Thomas Graham, whose experiments in gas effusion reinforced kinetic molecular theory and offered a mathematical relationship between relative rates of effusion and molar mass of a gas.

IDEAL BEHAVIOR

- Gases tend to be pretty well-behaved substances, and we can formulate laws that describe them based on this so-called ideal behavior. Laws like Boyle's, Charles's, Gay-Lussac's, and even the combined and ideal gas laws can be used to approximate the behavior of just about any gas or mixture of gases that we can imagine.

- But why are we able to come up with these all-encompassing gas laws that seem to apply well to a vast array of gaseous materials?

- Gases form when the atoms or molecules in a substance have sufficient kinetic energy to overcome the attractions that these particles naturally have for one another. When this happens, the gas particles have free run of their container, moving in random directions independently and at great distances from one another (at least on the molecular scale).

- These remarkably consistent behaviors stem from the fact that most gas molecules are extremely small, move extremely fast, and do not interact with one another—or at least any interactions are negligible because of their speed. It's this ideal behavior in the gas phase that makes the behavior of gases so predictable.

ROOT-MEAN-SQUARE VELOCITY

- How fast are gas particles moving, and what factors affect their speed? The answer depends on a few factors.

- Let's start by considering a single gas particle. If we could isolate it in a container, it would look like a randomly moving particle with a constant velocity. But we rarely, if ever, encounter a lone gas molecule in nature or in the lab. We usually run into them in huge groups of moles of atoms, so how do we account for this when it comes to how gases move?

- To describe the energy contained in a single gas molecule, we could use the same type of equation that a physicist or engineer would for a large object: $E = (½)mv^2$. This equation can be rearranged so that the velocity of the particle is a function of its kinetic energy and its mass—more accurately, the square root of the kinetic energy and the reciprocal of the square root of the mass.

- The linchpin of this idea of kinetic molecular theory is that molecules are in motion, especially in the gas phase. Gas molecules are constantly moving, in random directions, but they're not all moving at exactly the same speed. The motion of the molecules in the gas phase is somewhat random, but it's distributed statistically. We report on this speed as a root-mean-square (rms) velocity, which is a statistical average.

- We also know that the temperature of a gas is just a reflection of the kinetic energy that its molecules carry, so this leads to the conclusion that the velocity of a gas molecule depends on 2 things: its temperature and its molecular weight.

- By observing the same exact gas at different temperatures, we are essentially removing the influence of molecular weight and just observing the influence of temperature.

- It turns out that the rms velocity of a gas sample is proportional to the square root of the absolute temperature. If the absolute temperature of a gas sample is quadrupled, that means the rms velocity will double. This relationship sets us on our way to coming up with a calculation that describes the average motions of gases in a useful way.

- To make comparisons between temperature and rms velocity, we have to set the stipulation that the molecular mass of the 2 gas samples is identical. This is simple when the 2 samples are the same gas, but if they aren't, we need to account for the effect of molecular mass.

- We can keep temperature constant to study the effect of mass on rms velocity. The relationship between the molar mass of a gas particle and its rms velocity is also a square root—just like with temperature—but this time it's 1 over the square root of the molar mass. This is the relationship that allows us to predict how fast things will be moving based on their molar mass. We have to cut the mass by a factor of 4 to increase the rms velocity by a factor of 2.

- Combining the 2 proportionalities involving temperature and molar mass in relation to rms velocity, we realize that the rms velocity is proportional to the square root of the temperature over the square root of the molar mass for any gas at any temperature.

- When we run a few experiments, we can determine the proportionality constant, which is the square root of 3 times R, the ideal gas constant. This leads to an equation where we can get the actual rms velocity; it's equal to the square root of 3 times the ideal gas constant, times the absolute temperature (T) of the sample, divided by the molar mass (M) of that sample:

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}\,.$$

- Using that equation, we can determine the rms velocity (v_{rms}) for a given gas at a given temperature.

GRAHAM'S LAW OF EFFUSION

- At a given temperature, heavier particles move slower, on average. Scottish researcher Thomas Graham put this notion to the test when inspired by a colleague's observation that helium escaped a leaking container faster than the atmosphere found its way back in to replace it. This observation means that very small helium atoms seem to escape their container faster than molecular oxygen and nitrogen, each more than 8 times more massive.

- The process of a gas escaping its container through the walls is known as effusion. Graham immediately noticed a strong relationship between the molecular mass of a sample and the speed with which it escaped by effusion.

- In the process of effusion, a sample of gas escapes its container through microscopic pores in that container. Gas molecules are extraordinarily small in comparison to the size of even the tiniest pore in the container. To get out through a hole, all they have to do is randomly find that opening. After enough time, the process of effusion is good enough to get the entire sample of gas to escape.

- Consider that gases of varying sizes are known to have different rms velocities—specifically, lighter gases have a higher rms velocity. This means that a faster-moving gas sample will have more collisions with the wall than a slower-moving sample, and this means more opportunities to randomly find the opening and exit.

- Graham set to measuring the rate at which gases escaped vessels through porous materials. Not only that, but the correlation was mathematical, and it suggested that average particle speed was the driving force.

- Graham's law of effusion states that the relative rates of effusion of 2 gases is proportional to the square root of the ratio of the molar masses of the 2 gases:

$$\frac{\text{rate}_1}{\text{rate}_2} = \sqrt{\frac{M_2}{M_1}}.$$

- We can use Graham's law to predict the relative speed with which just about any 2 gases will escape a porous container. Water, which is 9 times more massive than hydrogen, escapes its container at ⅓ the rate of hydrogen. Oxygen, which is 16 times more massive than hydrogen, escapes its container at ¼ the rate of hydrogen. Clearly, atomic mass plays a role in governing the rate of effusion.

- Why does Graham's law work so well? The answer lies in our original assumptions about ideal gases. We assume that gas particles are extremely small and moving in random ways, independently of one another. If we add to that the new concept that rms velocity is a function of the mass of the gas particles, it begins to become clear what is happening.

- Faster-moving gases have a better chance of finding the opening more quickly, causing them to effuse faster. If a gas moves twice as quickly, it should escape the container twice as quickly, too.

VAPOR EFFUSION ENRICHMENT

- Graham's law relating molecular mass to effusion rate was a profound realization, because it allows us to intelligently construct facilities that can separate gases based on little more than a difference in their molecular masses.

- Graham's law of effusion tells us that if we can get uranium into the gas phase, we should have 2 types of gas particles: one having uranium-235 and the other having uranium-238. The technique of gas effusion was used in the 1940s and 1950s to acquire the material needed for nuclear devices. Government scientists developed a way to make a gaseous material from uranium by reacting it with fluorine gas to produce uranium hexafluoride.

- The vapor effusion method of enrichment was critical to the development of technologies that not only brought World War II in the Pacific theater to its historically abrupt end, but also helped power the homes and businesses of millions. The clever application of Graham's law launched the nuclear age by providing a way to get the isotopically enriched material needed for these applications.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 420–427.
Masterton and Hurley, *Chemistry*, 5.6–5.7.

QUESTIONS

1 Gaseous molecules move much faster than do those in the liquid phase. Evaporative cooling is a phenomenon in which gaseous molecules escaping a liquid into a higher energy state leave a colder liquid behind when they do so. How can kinetic molecular theory be used to explain the phenomenon of evaporative cooling?

2 Based on kinetic molecular theory, should separation by effusion work better at higher temperatures or lower temperatures?

3 Sulfur hexafluoride (SF_6) has a molar mass of 146 grams per mole. Oxygen gas has a molar mass of 16 grams per mole. How much faster will oxygen effuse from a porous vessel containing both gases?

Answer
3) about 3 times faster.

Liquids and Their Properties

LECTURE 24

This lecture will cover some of the more familiar properties of liquids that can be observed in the macroscale world. Specifically, you will learn about the properties of viscosity, volatility, vapor pressure, compressibility, and miscibility. Although you have probably observed examples of all of these many times in your life, this lecture will inject some insight into what is happening at the molecular scale that endows many of the most familiar liquids from your everyday life with their own unique set of properties.

INTERMOLECULAR FORCES IN LIQUIDS

- The most common intermolecular forces in pure substances are London dispersion forces, which are attractive forces based on intermittent dipoles, which form as electron clouds flex and shift around molecules and atoms; dipole-dipole interactions, in which permanent charge separations caused by differing electronegativities in bonded atoms create an electrostatic attraction; and hydrogen bonding, the ever-so-tenuous bond that can form between molecules with an O-H, N-H, or F-H bond within them.

- In gases, we often assume that these intermolecular forces are negligible and that molecular motion, or kinetic energy, is able to completely overcome them. Just like gases, liquids can experience all of these forces between and among the molecules and atoms that make them up.

- But the defining difference between liquids and gases is that in liquids, all of the molecules in a sample are in constant contact. This is because in liquids, those intermolecular forces are too strong for the molecules to overcome. This is about as nonideal a behavior as one can imagine.

- Because of this, intermolecular forces in liquids cannot be ignored like they are in gases, even under the best of circumstances. We can no longer assume that all samples will act exactly the same regardless of composition. There will be no "ideal liquid" laws.

VISCOSITY

- Viscosity is best defined as resistance to flow. If we were to invert similar-sized bottles of water and motor oil, the bottle of water would empty out first, and the oil would pour out in a slower, lazier process. The reason is that motor oil is more viscous than water. It resists flowing out of the bottle under the force of gravity, so it takes longer to escape.

- Viscosity is a crucial property of liquids used in certain applications. From machine lubricants to magma in the Earth's subsurface to the blood in your veins, flowing liquids are a part of nearly every natural or manmade system that we can study.

- One parameter that makes a liquid more or less viscous is temperature. To a chemist, temperature means kinetic molecular energy. So, lower temperature means slower-moving molecules and atoms in a liquid sample. This tendency of molecules to move more slowly at low temperature means that they can glom onto one another more effectively under the influence of their intermolecular forces. This makes them more resistant to flow as they cool down.

- But there must be more to viscosity than just temperature. After all, there are certain vital products that have differing viscosities at the same temperature—for example, gasoline and motor oil. Gasoline is a very "thin," easily flowing liquid, which it has to be so that it can be pumped easily through fuel lines into an engine. Motor oil, on the other hand, is "thick" and viscous. Motor oil's higher viscosity is critical to its ability to cling to internal parts of an engine and provide lubrication to that motor.

- The London dispersion forces in a sample of motor oil are much stronger than they are in a sample of gasoline. This gives each component the right viscosity for their job.

VOLATILITY

- Humidity is simply water vapor in the air around us. The more water vapor, the greater the humidity. In regions close to liquid water—such as lakes, swamps, and the ocean—there usually seems to be enough in the air (sometimes too much). But in areas with less liquid water around, there isn't much water vapor in the air.

- But water can only boil at 100° centigrade near the surface of the Earth. Even the hottest desert in the world doesn't approach that temperature, yet visit Washington DC on an August day with temperatures in the range of 30°C and you will not be able to mistake the water vapor in the air. The key to understanding the source of this humidity is in understanding a phenomenon called vapor pressure.

- Kinetic molecular theory suggests that molecules and atoms within a sample are moving at an rms, or average, velocity that depends on their temperature. But it also reminds us that the actual velocities of individual particles in the sample vary. A few are moving much faster than the rms velocity, and a few are moving much slower.

- The same is true of liquids. Molecules in liquids may be packed in together tightly, but they can still rotate and move within a sample. This is what allows a liquid to take on the shape of its container. But it has another effect, as well.

- Increasing the surface area allows more water molecules to escape. Similarly, raising the temperature increases the kinetic energy within the molecules, which explains why we find so much moisture in the air around our nation's capital every August.

- The tendency and speed with which a substance vaporizes is called volatility. As opposed to the colloquial meaning of the word "volatile," to chemists it simply means "vaporizes quickly and easily." Liquids with weaker intermolecular forces tend to vaporize more easily, even below their boiling points.

VAPOR PRESSURE

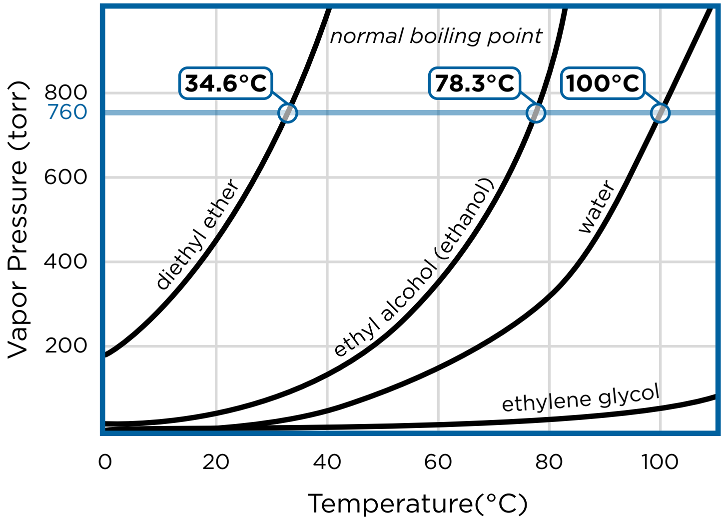
- Volatility is a handy concept, but it is only qualitative. We can say that one liquid is expected to evaporate more rapidly than another, but by exactly how much? A more quantitative way to measure this phenomenon is with vapor pressure.

- Consider a beaker filled with liquid water. We now know that a few of those water molecules can escape the liquid sample and reach the gas phase because of their individual kinetic energy. If we keep that water at the same temperature, the rms velocities of the remaining liquid molecules will redistribute, and more water molecules will escape in a steady process known as evaporation.

- But what if we instead closed the system so that no water vapor could escape? In this new scenario, a few water molecules can still escape into the head space of the flask, but they will eventually randomly find their way back to the surface and into the liquid again. As more water molecules reach the vapor phase, more return to the water, until there is no net change anymore. For every molecule that escapes, another one is captured, and a stable quantity of vapor is now present.

- If we were to do the same with ether at the same temperature, we would expect more ether to reach the gas phase when this balance is achieved because the molecules don't cling to one another as well. The result is a higher pressure within the sealed flask containing the ether. This pressure is called vapor pressure, and it gives us a solid numerical value with which to describe the volatility of any given compound.

- Vapor pressure also changes rapidly with temperature. This is the origin of the differing boiling points of liquids. When the vapor pressure of a liquid is equal to the applied atmospheric pressure, the vapor can now form not only at the surface of the sample, but also deep within the liquid, creating the rolling bubbles that we commonly associate with boiling.



- When the pressure against which the solvent is working is equal to 1 atmosphere, this temperature is called the normal boiling point of a liquid, which is yet another numerical value that we can link to a liquid's vapor pressure.

COMPRESSIBILITY

- The closeness of molecules in liquids, combined with their ability to shift and fill the shape of a container, gives them some remarkable properties, quite different from gases. Not the least of these differences is in density. Because of how closely packed liquid molecules are, their densities are often thousands of times greater than the same substances in the gas phase.

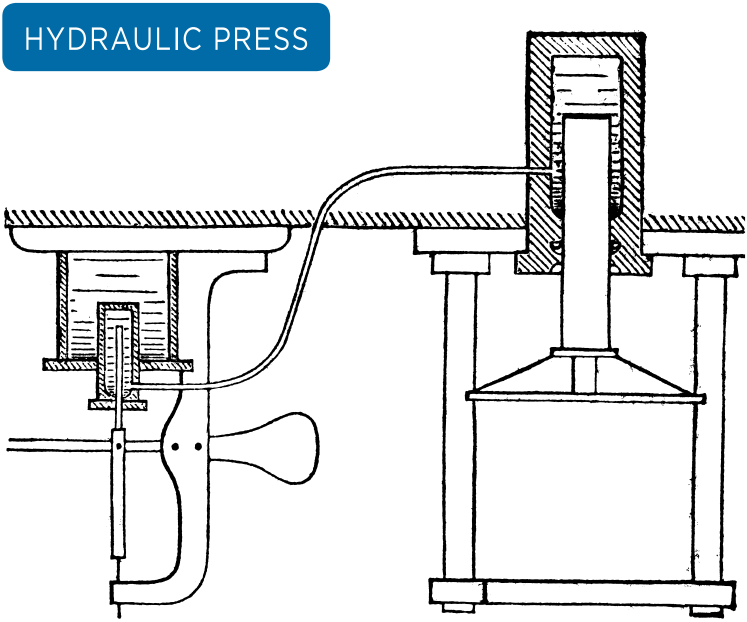
- For example, water has a density of 1000 kilograms per cubic meter. By contrast, the air you breathe has a density of just 1.2 kilograms per cubic meter. That is a tremendous difference in mass for the same volume of material. Add to this the fact that liquids can flow and take on the shapes of their containers, and it is easy to see why they are often used as a means of transferring force in all kinds of technologies, such as the classic water wheel.

WATER WHEEL

This brilliant invention, which relies on both the mass of water and its ability to flow as a means of transferring power to grain mills or other applications, was invented by ancient Greek, Chinese, and Indian civilizations—all 3 of which conceived this design independently.

- But the real magic happens when you consider not only the mass and ability to flow, but also the fact that packing molecules so closely together makes liquids incompressible. This means that unlike gases, liquids cannot change their volume in response to pressure. Instead, when a liquid is exposed to pressure, it has no choice but to pass that pressure along. This is the founding principle upon which the hydraulic press was built.

HYDRAULIC PRESS



In 1795, an English locksmith named Joseph Bramah filed for a patent on this device, which consisted of 2 closed pistons filled with a liquid. By exerting pressure on the smaller piston, the incompressible liquid inside must transfer that force, rather than absorb it. The larger that second piston is, the greater the force it will exert—in much the same way that a lever can amplify force at the cost of travel.

- The braking system in your car consists of a pedal, which activates a small cylinder attached to a brake line. That brake line is filled with a special fluid, which is designed to maintain the same lack of compressibility across a broad range of conditions.

- As you press the pedal, that liquid has nowhere to go, so it presses against the brake calipers or drum at the other end of the line. Being much larger than the piston at your brake pedal, those pads squeeze down with tremendous force—enough to stop a speeding car in its tracks.

MISCIBILITY

- Yet another property of liquids that is of importance is the concept of miscibility, which can be thought of as a description of how well one liquid dissolves into another liquid.

- Again contrasting liquids to gases, we always assumed that each gas would uniformly take on the entire volume of a container, mixing thoroughly with all other gases, regardless of their identity. But liquids are set apart by the fact that molecules in the liquid phase are very close together and interact with one another very strongly. Sometimes this interaction is favorable; sometimes it is not so favorable.

- Water and beverage alcohol, also called ethanol, look somewhat similar at the molecular level. Both are polar, have the critical O-H bond needed for hydrogen bonding, and are fairly small in size. This means that water and ethanol molecules can interact with one another almost as strongly as they do with other molecules of the same type. So, when mixed, they blend together to form a single uniform mixture of alcohol and water.

- Motor oils are large molecules consisting of mostly hydrogen and carbon, with few polar bonds and little hydrogen bonding capability, if any. Instead, motor oils are held in the liquid phase by powerful London forces generated by their immense electron clouds. Because the molecules in motor oil want to stick to others based on London forces, but water is held in the liquid phase by dipole interactions and hydrogen bonding, we don't expect water to interact well with the oil.

- The oil and water would rather cling to molecules of their own kind than one another. The result is called a biphasic liquid—one in which there is a lower-polarity oil phase and a higher-polarity water phase. They simply won't mix because they don't interact well.

- The miscibility of liquids tends to improve as the molecular structures of the compounds making them up becomes more similar. This is why you can mix gas and oil, but it's also why you have to shake a vinaigrette and pour it quickly before the layers of oil and water are able to separate from one another.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 444–445, 459–462.
Masterton and Hurley, *Chemistry*, 9.1.

QUESTIONS

1 Based on your knowledge of intermolecular forces, why is octane almost twice as viscous as isooctane at similar temperatures?

2 Based on the observation that a shock wave can be transmitted through a liquid, is it accurate to suggest that liquids are absolutely incompressible?

Metals and Ionic Solids

LECTURE 25

The time has come in our tour of matter by phase to move on from gases and liquids and consider solids. As you will learn in this lecture, solids are all about holding atoms, molecules, and ions together in close contact. You will learn how small structures can be packed together, and you will investigate the concept of the unit cell. In addition, you will learn how to classify and describe how atoms might pack themselves together.

SOLIDS

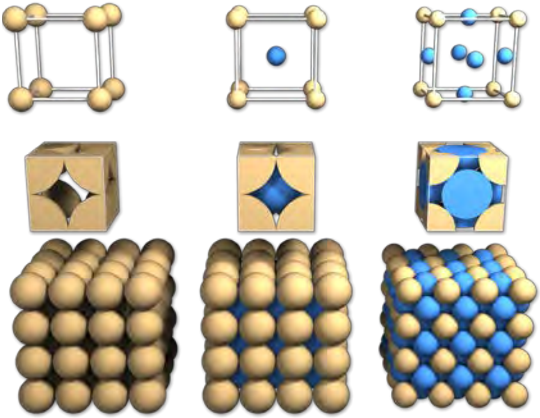
- We know that solids have defined volume and shape from our everyday observations. But what is it about solids at the atomic and molecular scales that gives them those properties?

- The reason for this is that the molecules, atoms, and ions that make up solids are locked in place by attractive forces so strong that these atoms, molecules, or ions lack the kinetic energy to overcome those forces.

- When this happens, a new consideration arises. Because their molecules, atoms, and ions are locked in position within them, solids can be highly ordered. When they are, we call them crystalline solids, and their high degree of order means that many of them have remarkably regular structures for us to study.

CRYSTALS AND THE UNIT CELL

- A crystal lattice is best defined as a repeating geometric arrangement of atoms or molecules in space. For example, consider gold atoms in their crystalline form. This solid has a highly ordered, repeating structure. Gold atoms aren't simply mashed together in random positions; instead, their locations regularly repeat, creating predictable patterns in the array of atoms. This arrangement is the crystal lattice of gold.



- But if crystal lattices go on and on forever, how do we draw one? We don't have enough ink, paper, or time to draw the lattice, even of a crystal so small it would fit in our hand.

- But the repeating nature of the lattice makes this an easy problem to solve. We can simply discuss what is called a unit cell, which is the simplest repeating arrangement of atoms that can describe a crystal lattice unambiguously.

- If we can identify a unit cell at the atomic level for any given crystal, then chemists can simply recreate the structure of the crystal by tessellating those unit cells together.

METALS

- Probably the best way to begin to understand how the symmetrical arrangement of atoms can impact a material is to consider one of those materials. Metals, which make up about ¾ of the elements in the periodic table, are common in our lives. In our homes and vehicles, hospitals, and even nature, examples of metals are all around us.

- Metals are some of the most useful elements because of certain properties that they all share. They all conduct electricity and are malleable to an extent, meaning that they can be bent or molded into shapes and pulled into wires to satisfy their intended purpose.

- Many elements are metals. But all of those metals aren't created equal. They may have a few similarities, but from the miniscule lithium atom to the massive, radioactive actinide series elements, metals offer a menu of elemental compositions that is unrivaled by any other type of chemistry.

- Although nearly all metals are solid at temperatures that we commonly experience on Earth, there are a few exceptions, including mercury. Some metallic elements are notably soft, such as copper. Others are incredibly hard, such as titanium and chromium.

- In the phenomenon of metallic bonding, atoms of metals come together to form closely packed clusters with a valence band that allows the valence electrons of those atoms free run of the entire matrix of atoms. Metallic atoms can take on various geometric arrangements when they come together to form a metallic solid. Let's consider crystal lattices and unit cells in general, using a simple 2-dimensional representation of what might be atoms in a lattice.

- A sphere is a shape that is impossible to tessellate. Even though atoms aren't really spheres—they have very complex structures and geometries within them—let's assume that they are for now. When we want to pack spheres into space as efficiently as possible, there are a few different arrangements that we could try. Two of the most commonly observed arrangements are squares and hexagons.

- Description of a 2-dimensional unit cell requires that we report on 3 things: the length of the 2 sides and the angle between them. We often use the notation a and b for the 2 sides and the Greek symbol alpha (α) for the angle between them. So, when a and b are equal and α is 90°, we have a square unit cell.

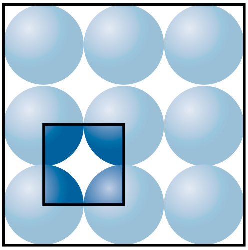
- When we change α to 120° but keep a and b the same, we create unit cells that are more closely packed together. These are hexagonal unit cells, whose name might seem strange because they have only 4 sides. But an atom in the associated lattice actually has 6 nearest neighbors around it. This is the source of the sometimes-confusing name.

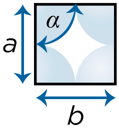
- There are 3 other general arrangements that exist in 2 dimensions: the rectangular, the oblique, and the centered rectangular formations. In a rectangular arrangement, we have a unit cell where a is not equal to b, but α is equal to 90°. In an oblique arrangement, nothing is equal: a is not equal to b, and α is not 90° or 120°. In a centered rectangular arrangement, a is not equal to b, but α is equal to 120°.

- So, the total realm of possibility in 2 dimensions is comprised of just 5 lattices: square, hexagonal, rectangular, oblique, and centered rectangular formations. But if we are going to use this concept in the real world, we're going to have to consider all 3 dimensions.

SIMPLE 2-D UNIT CELLS

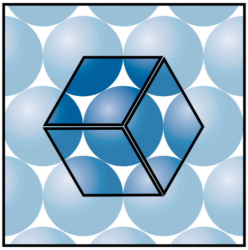
SQUARE

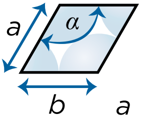




$a = b$
$\alpha = 90°$

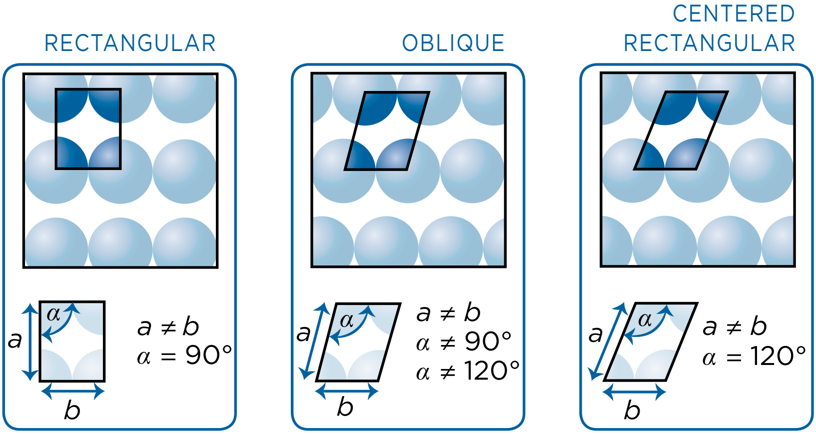
HEXAGONAL





$a = b$
$\alpha = 120°$

MORE 2-D UNIT CELLS



3-DIMENSIONAL LATTICES AND UNIT CELLS

- Our simple 2-dimensional representation helps us understand the basic concept of unit cells and the great variety of symmetries that they can produce even in just 2 dimensions. But we live in a 3-dimensional world, so to properly describe crystals, we need a third dimension.

- If we introduce to the square unit cell a third dimension, *c*, it creates 2 new angles, beta (β) and gamma (γ). Varying the edge lengths of *a*, *b*, and c, as well as the angles α, β, and γ, a total of 14 distinct 3-dimensional unit cells can be created. These can be organized into 7 general classes of lattices: cubic, hexagonal, trigonal, tetragonal, orthorhombic, monoclinic, and triclinic.

- The arrangements described by these 14 unit cells are called Bravais lattices, named for Auguste Bravais, a French physicist who correctly identified these 14 cells in 1848.

CUBIC UNIT CELLS

- When all lengths are identical and the angles are all held at 90, the resulting unit cell defines a cube, so crystal lattices described by this unit cell are called cubic crystals. Many metals have cubic crystal lattices.

- The cubic unit cell makes up 3 of the 14 Bravais lattices. How is that possible? Isn't a cube just a cube? Not exactly. Sometimes it isn't about the box; its what's inside that matters. The 3 cubic cells—primitive, body-centered, and face-centered cells—are all indeed perfect cubes with atoms at each corner. But they each describe a very different arrangement of atoms overall.

- Many solid metals tend to form cubic unit cells. In a cubic unit cell, all sides are equal in length and all angles are 90°. So, if we were to take 2 square arrangements of atoms and stack them directly on top of one another, we would get an arrangement that is perfectly cubic in all ways. Eight atoms each define a corner of the unit cell. It is simple and geometric, but also primitive.

- This simple arrangement is called a primitive cubic cell. The problem with this arrangement is that it produces a crystal in which each atom has just 6 nearest neighbors with which to share its metallic bond. In this arrangement, only 52% of the available space within the unit cell is filled by the spheres. Contact is minimized, and the effectiveness of the valence band is reduced. This arrangement is so poorly suited to metals, in fact, that only one metal, polonium, is known to adopt it.

- If we instead take those 2 square planes of atoms and pack them one on top of the other, but not directly on top, this offsets the second layer so that its atoms rest in the spaces left by the first square layer. We can then add a third layer, offset from the second, and directly above the first. This creates a denser structure, but it changes the spatial relationships among the atoms.

- So, layers 1 and 3 are positioned directly above and below one another, making up the boundaries of the cubic unit cell. But the atoms of the second layer aren't at the corners anymore; they are centered within the unit cell defined by the first and third layers. We still have to account for them, though, so this arrangement is called a body-centered unit cell.

- Body-centered unit cells have atoms with 8 nearest neighbors instead of 6. This means that a better metallic bond can form. Also, this arrangement has 68% of its volume as atoms—less empty space. This is a significant improvement over the primitive cubic cell. More contact among atoms means more stability, and we find that many metals, including all of the alkali metals, adopt this type of lattice.

- But we can do even better. Hexagonal packing makes for a more compact 2-dimensional array of atoms. When we use hexagonal layers, we can still find a way to stack layer 2 staggered to layer 1, and layer 3 can find a way to rest staggered to both layers 1 and 2.

- The simplest unit cell in this structure is still a cubic unit cell, but on each of the 6 faces, an atom is bisected. This is called the face-centered cubic unit cell. And although this means only 6 nearest neighbors, there are also another 8 neighboring atoms very close by. This increases the overall contact even more and reduces empty space.

- In a face-centered cell, 74% of the available space is occupied by the spheres. This is geometrically the best filling of space that can be achieved using spheres. It maximizes contact among atoms, creating a valence band with tons of overlap. This is the arrangement of atoms in a number of familiar metals, including gold, silver, copper, nickel, aluminum, and more.

- All of these arrangements allow us to make sense of metals. No matter which form they take—primitive cubic, body-centered cubic, or face-centered cubic—their symmetry leads to vast networks of metallic bonds that help explain their crystalline properties.

ALLOYS

- Metals are amazing crystalline materials with diverse, useful properties. But sometimes even the buffet of pure metals afforded to us by nature simply doesn't yield a material with the properties that we need. When nature fails to provide just the right metal for a given application, that's when chemists come in.

- Just as nonmetals offer a potential list of ingredients to mix, forming a vast library of compounds, many metals can also be combined to create materials with new properties. Materials comprised of multiple metals are referred to as alloys.

- There are 2 general types of alloys: solid solutions and intermetallic compounds. Solid solutions are formed when 2 molten metals are mixed in just about any composition. The metal atoms may be thoroughly mixed overall, but their arrangement within the product are not highly ordered.

- In intermetallic compounds, a very specific ratio of metal atoms is combined into a new, highly ordered, and sometimes very complex lattice. Compounds like these tend not to be used so much for their strength as for other properties.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 464–475.
Masterton and Hurley, *Chemistry*, 9.5.

QUESTIONS

1. Metal alloys are sometimes heat-treated in a process called annealing. During this process, an alloy is heated to a specified temperature and cooled to achieve a desired separation of the metal constituents. If a high degree of separation is required, would a fast or slow cooling process be best?

2. Pure sodium chloride and pure potassium chloride have nearly identical melting points—about 1050 kelvin. An equal mixture of the 2 melts at a slightly lower temperature of about 950 kelvin. How can ionic bonding and crystal lattices be used to explain this phenomenon?

Covalent Solids

LECTURE 26

Metallic bonds are just one set of forces that can hold a solid together, and in this lecture, you will learn about some of the others. First, you will be introduced to ionic solids. Next, you will learn about molecular solids. Then, you will be exposed to a different kind of covalent solid: covalent network solids. Finally, you will consider a very common class of network covalent material, silicates, based on silicon dioxide.

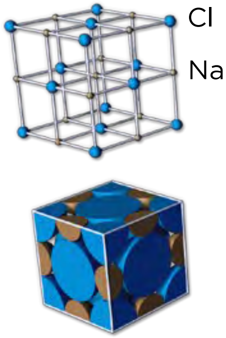
IONIC SOLIDS

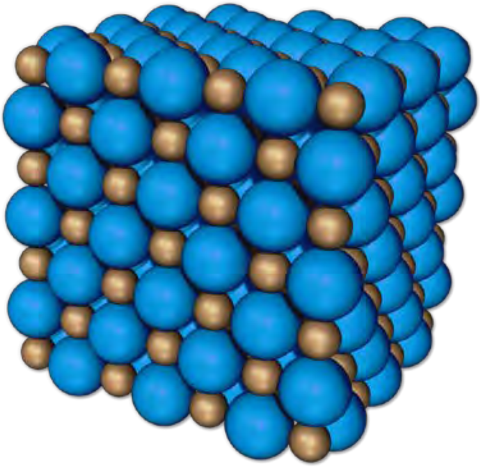
- In the phenomenon of ionic bonding, electron transfer creates charged particles known as ions that pull on one another with an attractive force due to their electrostatic charges. The formula NaCl, for example, conveys the ratio of each ion in the compound.

- But electrostatic attractions are not confined to any 2 specific sodium or chlorine atoms in a given molecule. A positively charged sodium ion will attract a number of chloride atoms around it in the solid, just as chloride will pull on many sodium ions.

- The total ratio of ions is 1 to 1, but there is no NaCl molecule to speak of. Instead, much like metals, ionic compounds tend to form crystals with great order in them. They do so not to spread out or optimize a valence band through which electrons can freely move, but to optimize attractive forces between and among a collection of ions that forms when electrons are transferred between atoms and held tightly in place in the resulting ions.

- For example, the crystal structure of sodium chloride allows us to easily assign a face-centered cubic unit cell to the crystal. Sodium ions fill the interstitial spaces that are left behind by the chloride ions. This is a good thing, because there would be no charge balancing if they weren’t there. But the sodium ions are along the edge of a unit cell, so they each only count for a quarter of each unit cell.





- Unit cells give us a great deal of information about ionic solids, including clues to their formula, density, solubility, and other properties. But ionic solids can become much more complex than the simple example of sodium chloride. Nature produces such a wide variety of elemental compositions and formation conditions that a litany of beautiful and useful ionic minerals form in locations around the globe.

MOLECULAR SOLIDS

- Molecular solids consist of discrete molecules, each of which is individually held together by powerful covalent bonds. In many cases, molecules of the same type arrange themselves into ordered arrays of repeating molecules, much like the atoms of metals or the ions of ionic compounds.

- But molecular solids are a bit different than their metallic and ionic counterparts, most notably when it comes to the magnitude of the forces holding them together.

- The atoms in most molecules are held by powerful covalent bonds, but unlike metals and ions, in which valence-band electron motion and electrostatic attraction form crystal-wide networks of attractive forces, the covalent bonds in molecules are very discrete and localized within each molecule.

- Each individual molecule is indeed held together by covalent bonds, but what holds all of those molecules together in solids? In most cases, the forces holding them together are the intermolecular forces: London dispersion forces, dipole-dipole interactions, and hydrogen bonding. These intermolecular forces are much weaker than a typical covalent bond.

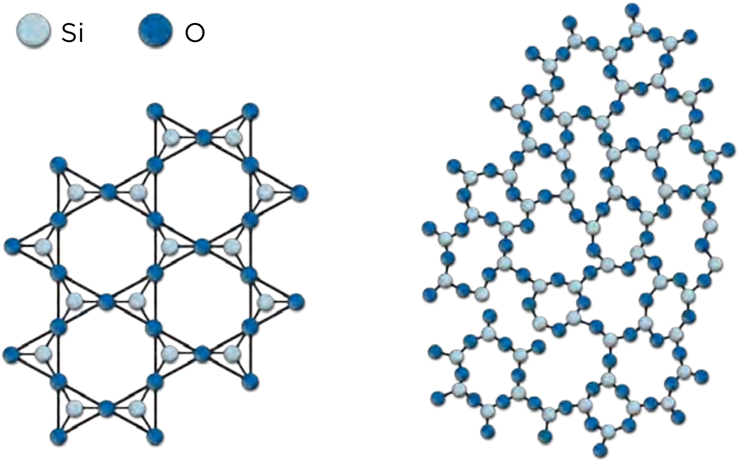
- Even when molecular compounds come together in a highly ordered crystal, the attractive intermolecular forces rarely come anywhere near to rivaling the attractive forces created by the electron sea in metals or by the network of ion-ion interactions in ionic compounds. Because of this, molecular solids tend to be relatively soft or brittle, melting at much lower temperatures than metals and ionic compounds.

- Despite being held together by much weaker forces than metals or ionic compounds, molecular solids nonetheless can have very strong tendencies to take on crystalline forms when they are in the solid phase.

NETWORK COVALENT MATERIALS

- A network covalent material is one in which covalent bonding is still the strongest force in play, but the covalent bond networks are not confined to individual molecules. The covalent bonding chains instead reach across huge networks of atoms, bonding the entire solid together with great strength.

- Glass is a network covalent material. It is a huge network of silicon and oxygen bonds that can reach for thousands upon thousands of atoms. Essentially, this makes a window one gigantic molecule of silicon dioxide, also known as silica.



crystalline SiO_2
(quartz)

amorphous SiO_2
(glass)

- If you have trouble identifying the unit cell of silica, it's because glass doesn't have any symmetry to speak of. It is a disordered group of silicon and oxygen atoms held tightly by covalent bonds that formed on rapid cooling from the liquid phase, locking those atoms in place. Yet even without a defined crystalline structure, glass is hard enough that we make windows, beverage containers, and optical lenses from it.

- We can rely on glass to hold its shape well once it is cooled rather quickly. If we cooled glass a bit more slowly, we could make a crystal of silicon dioxide. The slow cooling of molten silica—the same material used to make glass—instead makes quartz.

- Quartz is a crystalline mineral form of SiO_2, one in which the atoms have had time to find their perfect fit within the network covalent structure. The critical slow cooling leads to a crystalline solid instead.

- This is why quartz is so often found in geological settings. In subterranean geological settings, molten silica can sometimes take centuries or even millennia to cool and solidify. This gives the atoms within all the time they need to find their perfect position and create this.

- It is a hexagonal crystal form. There are actually 2 major crystalline forms of quartz. They have very subtle differences in their crystal structure, but both hail from the hexagonal group of Bravais lattices. Quartz tends to form beautiful, symmetrical prisms with hexagonal bodies.

- The lack of any symmetry in silica and the complete symmetry in quartz interestingly gives them both a property that not all minerals share. When a crystal with planes of weakness forms—such as a metal, or the ionic compound sodium chloride—that material tends to break along the plane of weakness under stress.

- This process usually creates a clean break, forming a new face that is consistent with the crystal morphology of the sample. This property of a material is referred to as cleavage by mineralogists.

- But because of its complete lack of order, glass does not have a well-defined cleavage. Instead, it more often undergoes a different process, called fracture, when struck. Quartz, for the exact opposite reason, does the same thing. Its highly ordered network covalent structure does not have any significant planes of weakness either.

- Instead, when glass, quartz, and other minerals like them break, they tend to display what is known as conchoidal fracture. This curious property creates curved, bowl-shaped features on the recently broken glass or quartz. This is part of what makes broken glass so dangerous. When 2 curved conchoidal fractures meet along an edge, the result is a very sharp edge.

SILICATE MINERALS

- Nature creates many minerals with properties that fall somewhere in between those of purely network covalent and purely ionic compounds. Even the glass that you very likely have in your cupboard isn't really pure silica. It is often what is known as soda lime glass—a glass made by combining pure silica with sodium oxide (hence the "soda") and a bit of calcium oxide (also called lime). A bit of aluminum oxide is also often included in this formula.

- This process serves to introduce a few sodium, calcium, and aluminum ions into the matrix of the glass, giving it more desirable molding and cooling properties at the cost of a certain amount of durability. So, most of the glass that you encounter on a daily basis is actually what is called a sodium-calcium alumino-silicate material.

- Geologists have a different name for—and a different perspective on—this chemical combination. They call it plagioclase feldspar.

- Silica is a highly abundant material near the surface of the Earth—so abundant that it serves as something of a solvent for a number of less abundant metals. In doing so, silica provides a basis for a number of rock-forming minerals and even gemstones.

- Sodium, calcium, and aluminum are also fairly common in the crust of the Earth, and they often combine with silica in somewhat the same way that they do in soda lime glass.

- The difference again is that cooling on the geological time scale allows these combinations to form crystals with highly ordered covalent bonds. Imagine quartz, but substitute one aluminum atom for every fourth silicon. Aluminum is short by an electron, so forming the analogous structure with 4 bonds to oxygen leaves the structure with a net negative charge.

- Of course, that can't happen all by itself in nature. There has to be something there to balance out that charge, and that is where sodium and calcium come in.

- Take the example of sodium. In its ionic form, it is commonly a sodium ion with a single positive charge. By participating in bonding with some of the oxygen atoms in the silicate, sodium helps to attenuate this charge and influences the geometry of the crystal. This creates a mineral with a formula of $NaAlSi_3O_8$, also known as albite.

- Calcium can also act in this way, balancing 2 aluminum atoms in the silicate structure around it. This gives it a formula of $CaAl_2Si_2O_8$, also known as anorthite.

- Albite and anorthite make the 2 so-called end members of plagioclase feldspars. When differing amounts of sodium, calcium, and aluminum are incorporated into cooling magma, plagioclase feldspars of various color, hardness, and crystal habit can form.

- Plagioclase feldspars are extremely common rock-forming minerals found in the crust of the Earth, and they owe their appearance, hardness, and overall chemistry to the very special network of aluminosilicate bonds holding them together.

- The universe has provided Earth with many other metals that have to be considered to truly understand how rock-forming minerals vary in their behavior and properties. Magnesium, iron, beryl, and others can find their way into similar structures, producing new series of minerals with their own complex structures and properties.

- These systems are so complex and so vital to the geological machinery of the Earth that an entire science of minerology has been devised around them. These sophisticated solids can combine network covalent, ionic, and even metallic bonding behavior all into a single incredible class of solids with wonderfully diverse properties: silicate minerals.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 470–474.
Chemjobber, "Puzzling Polymorphs."
http://www.chemistry-blog.com/2010/06/07/puzzling-polymorphs/.
Masterton and Hurley, *Chemistry*, 9.4.

QUESTIONS

1. Covalent solids can take on multiple solid crystalline forms with varying solubility. Once dissolved, however, are solutions produced from different crystal forms any different from one another?

2. Boron nitride is a covalent compound with a melting point greater than 3000 kelvin. Is boron nitride likely to be a covalent solid or a network covalent solid based on this observation?

Answer

2) Boron nitride is a network covalent solid. Its large network of covalent bonds must be broken for it to melt, explaining the need for such high-temperature conditions.

Mixing It Up: Solutions

LECTURE 27

In this lecture, you will learn what can happen when pure substances are mixed with one another thoroughly at the atomic or molecular level. These kinds of materials are called solutions. You will learn about the different ways of reporting solution concentrations and how chemists prepare solutions of known concentrations in the lab. Furthermore, you will learn how to determine the concentration of a solution, turning to the interaction of light and matter for the answer.

SOLUTIONS

- A solution is any homogeneous, or uniform, mixture of 2 or more substances. That homogeneity has to be at the molecular level for a material to truly be considered a solution. We encounter solutions every day, and a wide array of professionals—from chefs to pharmacists to engineers—create solutions that are used to make our everyday lives better.

- When discussing solutions, we call the more abundant phase into which other materials are dispersed the solvent. All of those materials that are dissolved are often called solutes.

- Most of the time, these definitions are adequate, because there is usually one overwhelmingly prevalent solvent, such as the water in a cup of coffee. But there are situations in which these 2 can become muddled, such as in cases like a bottle of vodka, which is about half water and half ethanol. These ratios can be very close to half and half.

- Although these are still considered solutions, the role of solute and solvent can be difficult to define in these examples, so we will stick to examples in which the solute and solvent are more easily assigned for now. Moreover, although solids (such as metal alloys) and gases (such as our atmosphere) also meet the strict criteria of solutions, we will confine our discussion to liquid solutions, by far the most commonly encountered solutions in chemistry.

SOLUTION CONCENTRATIONS

› Solutions are made by mixing at least one solute into a solvent. When preparing a solution, when we are dealing with a pure material, there is just that material to consider. For example, gold is always made strictly of gold atoms.

› But when we take the step up to solutions, things change. If we are dissolving one material into another, such as dissolving salt into water, there comes a question of proportions. Just how much salt has been dissolved into the water? There is a continuum of ratios among solutes and solvent, and we are forced to define this relationship if we want to discuss a particular solution.

› As chemists, we need to communicate exactly how much of each component of a solution is present. But what values should we use? Mass is easily measured in the lab using balances, so expressing concentrations using units of mass might be useful. Similarly, we can measure volume quite easily using a graduated cylinder, for example, so there might be times when volume is a good choice.

› But when molecules react, it is their stoichiometry that becomes most relevant, so depending on our discussion, we might want to use moles to convey how much solute is present.

› There are many options for reporting concentration, and several different units of concentration have become popular among chemists.

› A commonly used unit to express concentration in solutions is molarity, which is the moles in solute in a solution divided by the total volume of that solution in liters: $M = n/V$. This gives us a very easy way to combine the number of moles of something—which we might need to know, for example, for a stoichiometry problem—with a quantity whose volume we can actually measure.

› Another unit of concentration, which is often confused with molarity because they sound so similar, is molality (*m*). Molality has to do with the number of moles of solute divided by, not the liters of solution, but the kilograms of the solvent in which it is dissolved.

› We don't typically use molality in laboratory procedures because it's difficult to measure how many kilograms of the solvent we have when it's contaminated with the solute. Rather, molality will help us describe some very interesting properties of solutions.

› In addition to molality and molarity, sometimes when expressing concentration we need to know the mole fraction, or the relative number of moles of the solute divided by the total number of moles of compounds or molecules or atoms in a solution. Mole fraction is often used like molality; it allows us to predict certain properties of solutions.

› It's very rare that you would use mole fraction in a procedure, for example, in a laboratory, because nobody wants to count how many moles of solute there are. Molality and mole fraction are tied more to predicting physical properties, whereas molarity is what we typically use procedurally.

› In addition, we sometimes report solutions as mass percent. A mass percent unit is simply the mass of the solute divided by the mass of the solution, and then multiplied by 100 to make it a percentage. Think of it as a mass fraction, or a mass ratio. Mass percent is a very nice way to practically report on how to create a solution, because masses are things we can measure in the lab.

› Consider the fact that solutions can become extremely dilute, and when they do, things like mass percent might produce extremely small numbers that aren't that easy to work with. When that happens, we often use a different type of expression that we can modify to our needs: parts per thousand, parts per million, parts per billion, etc.

- In this type of nomenclature for concentration, we use the ratio of a solute mass to the total solution mass, but then we multiply by whatever number it gives us to get a reasonable quantity to work with. This type of unit can manifest itself as parts per thousand if we use 10^3, parts per million if we use 10^6, and parts per billion if we use 10^9.

- Molarity is useful for solutions near standard temperatures. Molality is particularly useful for situations in which solutions might expand or contract under the influence of temperature. Mole fraction helps us keep track of how many molecules of each component are in a solution. Mass percent and the related units of parts per thousand/million/billion allow us to describe extremely low concentrations when it is appropriate.

ELECTROLYTES AND NONELECTROLYTES

- How does a solid dissolve into a liquid, and what happens at the molecular level when this takes place? If we start with similar amounts of sugar, sodium chloride, and calcium chloride dissolved in water, conductivity testing shows that the sugar solution does not conduct, the salt solution does conduct, and the calcium chloride solution conducts even better. Is there something fundamentally different about how sugar and salt dissolve that creates this observable difference in their solutions?

- This same question haunted the famous Swedish physicist Svante Arrhenius. In 1884, he posed a new theory to try to explain exactly how certain compounds dissolve in water and why some create conductive solutions while others do not. His theory is called ionization theory: For most molecular solids to dissolve, they must interact well enough with the solvent that they are willing to give up the attractive intermolecular forces holding them together as a solid to interact with the solvent molecules instead.

- Sugar can do this quite easily, dissolving molecule by molecule. As each molecule of sugar dissolves, the intact molecule sacrifices the intermolecular forces holding the crystal together, but creates many new interactions between intact sucrose molecules and the water molecules in the solvent, including dipole-dipole attractions and hydrogen bonds.

- But what about salt? Sodium chloride is an ionic compound—a broad array of sodium and chloride ions held together by the attraction that their opposing charges create. There are no discrete molecules to be pulled away and surrounded by solvent molecules. Instead, the ionic compound must dissociate into individual ions, creating separate charged solutes.

- This is exactly what happens, and it gives us an explanation for why salt solutions conduct electricity so well. These dissolved ions are called electrolytes in recognition of their ability to propagate electrical current when dissolved in solution.

DETERMINING SOLUTION CONCENTRATIONS

- We can prepare solutions of known concentrations by carefully measuring the amount of solute, solvent, or solution involved, depending on our needs. But what happens when we need to determine the concentration of a solution that we didn't prepare?

- Fortunately, there are many properties of solutions that change predictably with their concentration. Some of these properties are refractive index, which measures how a solution alters the path of light, and absorptivity, which is a measure of how a solution absorbs light.

- When a straight object, such as a thermometer, is inserted into a fish tank, for example, the object looks partially submerged when viewed head on, but from a certain angle, it appears to break. What causes this strange bending of light, which is associated with refraction?

- It is a question of density. The speed of light is constant at 3×10^8 meters per second in a vacuum, but in truth it moves slightly slower in non-evacuated mediums. This slower velocity has no observable effect when the light is at a perfect 90° angle to the new medium that it is entering. But as the incident angle of the light becomes more and more shallow, we see a more distinct change in its path because it moves more slowly through the water than it does through the air.

- Although this phenomenon had been observed by ancient Greek and Indian civilizations more than 1000 years ago, the mathematical relationship between the 2 angles was not understood until it was sorted out by Willebrord Snell in 1621.

- You are probably more familiar with refraction than you think. It is the reason behind the classic desert mirage. As hot air expands and rises from the sand in the distance, currents and eddies of differing-density air masses mix and swirl. As light refracts at differing angles in the mixing air pockets, a shimmering effect is observed, which is often mistaken for a body of water in the distance.

- Chemists exploit this effect in a more controlled environment, using a device known as a refractometer. A simple refractometer uses a thin film of the solution to be analyzed sandwiched between 2 plates. As light passes through the solution film at an angle, it is refracted toward a viewing reticle, but only at specific angles.

- Refracted light reaches the reticle, but reflected light does not. This creates a defined horizontal line, the location of which in the reticle lets the viewer know just what the angle of refraction is.

- Refractive index gives us a way to determine solution concentrations by essentially measuring how the density of the solution impacts the path of light. The incident angle is proportional to the path difference.

- Another way that solution concentrations can be determined is by measuring the extent to which they absorb light, rather than how they refract it. This technique was developed in 1852 by German physicist August Beer, who observed that the amount of transmitted light decreased exponentially as the concentration of an absorbing solute increased.

- He mathematically converted transmittance into a unit called absorbance by taking its logarithm, allowing him to create a simple linear relationship between concentration and the absorption of light.

- If we know the molar absorptivity of a solute, we can carefully measure the intensity of a light beam before and after it passes through the solution and calculate the concentration of the solute in the sample.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 122–124, 144–151, 543–547.
Masterton and Hurley, *Chemistry*, 10.1.

QUESTIONS

1 Consider the possibility that certain substances ionize partially in solution, rather than completely or not at all, as were the cases with salt and sugar. What would you expect to observe during the lightbulb demonstration for such a solution?

2 If we were to reproduce our Beer's law demonstration still using red dye but with a red laser instead of a green laser, how would you expect the observations to differ?

Solubility and Saturation

LECTURE 28

In this lecture, you will learn about solubility and saturation. You will consider what makes so many salts and polar compounds soluble in water, as well as the maximum solubility of materials in water and the concept of saturated solutions. You will also investigate the effect of both temperature and pressure on solubility and the concept of supersaturation. Furthermore, you will learn how solubility and saturation can explain some of the most breathtaking natural features in the world.

SOLUBILITY

- Chemists use an idiom to help determine what dissolves in water and what doesn't: like dissolves like. This means that water, being a very polar substance, can form better interactions with polar, hydrogen-bonding, or ionic solutes like sugar or salt.

- The massive lattice energy that sodium chloride has is a measure of the energy needed to separate the ions in a vacuum. This amount of energy is tremendous. But put sodium chloride in water and just a little stirring is all it takes to completely disassemble the crystalline material. What makes the difference?

- The difference is that when an ionic solid dissolves, its constituent ions are dispersed not into the gas phase, but into the liquid solvent. Water, being so polar, can arrange itself around the ions in such a way that its dipoles stabilize the charges of the ions.

- When we add any solute to a solution, there comes a point at which it is impossible to encourage more of that solute to dissolve. Just like a sponge that can no longer absorb any more water, a solvent can and will reach a point at which it simply cannot hold any more of a particular solute. That point is called saturation.

- In the case of sodium chloride, saturation happens when we add 6 moles of salt to 1 liter of solution. So, sodium chloride solutions in water are saturated at just about 6 molar. We refer to this concentration—the one at which the solution is saturated—as the solubility of the solute.

- Sodium chloride has a solubility of 6 molar, or about 350 grams per liter. That means that a completely saturated salt solution is about 26% salt by mass.

- The extremely high solubility of salts like sodium chloride is responsible for the high density of the waters in the Dead Sea, which is famous for being so dense that a human will float effortlessly on its waters due to the added buoyancy the salt provides.

- The Dead Sea reached this very high salinity because it has been slowly evaporating over millennia. The water in the sea is constantly lost to vaporization due to water's inherent volatility. But salts like sodium chloride are nonvolatile. They don't have any vapor pressure to speak of at ordinary temperatures and pressures. So, over long spans of time, as the volume of the sea decreased, its concentration increased until it reached the point of saturation.

- When this happens, water continues to evaporate, but the remaining salt that it can no longer dissolve comes out of solution in a process known as precipitation. The bottom of the Dead Sea is actually covered in a bed of crystalline salt material left behind by evaporating water. It simply can't get into the solution because that solution is saturated.

TEMPERATURE AND SOLUBILITY

- Steam cleaning is a great way to be sure that you get every unwanted bit of grit and grime off of a surface. Water itself isn't that great at dissolving many things—especially low-polarity materials that make up most of the dirt and grime that we want to get rid of.

- One could use water to rinse a carpet soiled with dirt or oil until the cows come home, and it is very unlikely to come clean. But heat that water to its boiling point and a quick pass with a steam cleaner usually takes care of the job in no time.

- Increasing the temperature of a solution can have a remarkable effect on its ability to dissolve certain materials that it usually can't. This makes sense if we think about dissolution in terms of free energy.

- Compare a sample of salt and water to the solution that it creates. Which has higher entropy? The solution does, because it is less ordered. So, our understanding of Gibb's free energy helps us understand why heating water helps it dissolve solids better in general. Increasing the influence of entropy increases the overall spontaneity of the dissolution process in this case.

- In the case of gases, the opposite is generally true. A gas-phase solute, such as carbon dioxide dissolved in a soda, would have a higher entropy when it is not dissolved in a liquid, because out of solution, a process known as degassing, or effervescing, creates a gas from a liquid solution. So, increasing the temperature of solutions in which gases are the solute can actually decrease their solubility.

- You can easily observe this the next time you boil a pot of water in your kitchen. You will notice that long before the water boils, small bubbles of gas form along the walls of the pot. This is not simply water vapor; it is the dissolved oxygen and nitrogen gases in the water coming out of solution.

PRESSURE AND SOLUBILITY

- Higher pressures mean more gas molecules being squeezed into contact with the surface of a solution—a process that allows that solution to absorb even more of the gas than we might normally expect.

- The relationship between pressure and solubility is known as Henry's law, which states that the solubility of any gas is proportional to its overall pressure above the resulting solution: $S_g = kP_g$. The proportionality constant, *k*, from this equation is known as the Henry's law constant for any particular gas.

- Henry's law is a linear mathematical relationship. If we double the pressure, for example, we also double the solubility. Henry's law allows us to predict the solubility of a gas and how it will vary as we pressurize and depressurize that gas, above the solution.

- The bubbles in your beer or soda are a testament to Henry's law. An ordinary, well-mannered soda drinker will enjoy the slow, lazy cascade of bubbles over the course of an hour or so until the new state of saturation is reached in the soda, rendering it flat.

- If you are a bit more mischievous, you can accelerate this process by agitating the contents of the can, creating a number of small bubbles in the solution prior to opening it. These small bubbles act as nucleation sites, where dissolved carbon dioxide can come out of solution much faster. When you open it, the result is a mess, and whatever beverage you can salvage afterward is already flat in a matter of seconds.

- Even more dramatic than that result is the popular Coca-Cola and Mentos demonstration, in which the surface of the candy acts just like the bubbles in a shaken soda, but with even more immediate results. Based on Henry's law calculations, a gently opened 2-liter bottle of soda is primed to expel about 6 liters of carbon dioxide gas before it goes completely flat. Directing all of that gas through the narrow mouth of the bottle creates a remarkable and fun visual effect.

SUPERSATURATION

- Supersaturation is a metastable state in which the temperature or pressure conditions on a saturated solution have changed so that the concentration of solute is higher than the ordinary saturation level.

- A modern example of this is the nitrogenation of beers. Certain stout beers get their bubbles not from carbon dioxide, but from nitrogen, which gives the beer a different flavor and mouthfeel.

- But nitrogen behaves differently than carbon dioxide in another way. It tends to form a supersaturated solution when the beer is depressurized. That means no bubbles, no fun mouthfeel, and no smile on the beer drinker's face.

- So, inventive beer aficionados created the so-called widget. A widget in a can of stout has one purpose: to release a few small bubbles of gas when the can is opened, giving a nucleation site onto which the dissolved nitrogen in the beer can effervesce.

- Until the widget was invented, nitrogenated beer was only available in bars from special taps that create a turbulent flow in the brew as it exits. Both of these technologies essentially shake up your beer for you to get that gas effervescing and enhance the experience.

CAVE FORMATIONS AND SOLUBILITY

- The stalactites, stalagmites, and even the body of caves all form because of the phenomenon of saturation. The rock in the Appalachian Mountain consists of a great deal of limestone, which is primarily composed of calcium carbonate, a rock-forming mineral that is soluble in water.

- Groundwater permeates these rocks, slowly dissolving the limestone rock, creating the cave formations that the Shenandoah Valley is famous for. But now, flowing through these caves is saturated solution of calcium carbonate.

- As that water makes its way through the subsurface, it encounters the roofs of other caves and has nowhere left to go but down a growing stalagmite. As a droplet of that solution reaches the end of the line, it can either cling to the stalactite or fall to the floor of the cave. In either case, as the droplet slowly evaporates, it reaches the point of saturation and has no choice but to deposit its cargo of solute on whichever formation it happens to be on.

- This process can be extremely slow, but knowing the temperature of the subsurface, rate of water flow, and the total solubility of limestone in that water allows scientists to estimate the ages of these stunning features and, in doing so, build a history of how and why these caves themselves form. It is an amazing geologic story spanning hundreds of millions of years, and it is all thanks to the most common solvent on Earth: water.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 530–543.
Masterton and Hurley, *Chemistry*, 10.2.

QUESTIONS

1. Water is just one of many compounds that can act as a solvent. What are a few other naturally occurring materials whose ability to act as a liquid solvent drives natural chemical processes?

2. When heating tap water on a stove, small bubbles tend to form along the interior walls of the pot long before the water reaches its boiling point. What gas or gases are these small bubbles made of, and why do they form?

Colligative Properties of Solutions

LECTURE 29

The uses for salt are remarkably varied because it is a simple, abundant, and safe chemical. Sodium chloride is used in so many applications because certain properties of solutions can be altered by dissolving whatever we choose in them. These properties are called colligative properties, and they depend on the overall concentration of dissolved particles in the solution. In this lecture, you will learn about some of these properties, including freezing points, boiling points, vapor pressure, and osmotic pressure.

CONCENTRATION AND TEMPERATURE

- Molarity is defined as the moles of solute divided by the number of liters of solution. If we heat a solution, the molarity will change. By heating a solution and causing it to expand, we're causing its volume to increase, which mathematically causes its molarity to decrease.

- If we're doing an experiment that involves a temperature change, we need to use a different unit of concentration from molarity that doesn't change as drastically with temperature, if at all. We need to use molality instead.

- Even in the face of expansion, molality doesn't change. This allows us to use this concentration over the broad range of temperatures that we're going to need to discuss things like boiling and freezing in the same context.

COLLIGATIVE PROPERTIES

- Certain properties of solutions don't depend on which solutes are present, only on how much. Of course, the flavor of a wine, the color of a dye solution, or the cleaning power of a detergent depend on the identity of the solutes they contain. But simpler, more fundamental properties like the freezing and boiling points of solutions are far less selective.

- Freezing points, boiling points, vapor pressure, and a curious property of solutions called osmotic pressure are referred to as colligative properties, named for the Latin term for "bound together." This term is used because the properties in question depend not on the identity of the solute in solution, but only on the concentration of the solute particles dissolved.

- When it comes to certain properties of dilute solutions, all that matters is the concentration of dissolved particles. They can be anything—molecules, atoms, or ions.

ELECTROLYTES AND THE VAN'T HOFF FACTOR

- Colligative properties depend only on the number of dissolved particles of solute, not necessarily on the identity of that solute. What does that mean for electrolytes (things like sodium chloride that become ions when dissolved)?

- The van't Hoff factor is the ratio of dissolved particles that we get per mole of actual solute that we dissolve. It can be estimated simply using stoichiometry of dissociation.

- Let's consider sodium chloride and compare that to magnesium chloride (another common salt) and sugar. When sodium chloride dissolves, 2 moles of ions form, which means that its estimated van't Hoff factor is 2: 1 for the sodium ions and 1 for the chloride ions.

- To estimate the van't Hoff factor for magnesium chloride, we have to acknowledge that we get 2 moles of chloride ions and 1 mole of magnesium ions. This means that its estimated van't Hoff factor is 3.

- When we consider the dissolution of sugar, a molecule that does not ionize appreciably when it is dissolved, the van't Hoff factor is 1. It's the identity operator because there is no dissociation. The concentration of sugar is the concentration of dissolved particles.

BOILING AND FREEZING POINTS

- The first 2 colligative properties go hand in hand. They are the freezing point and boiling point. It was long known that the freezing point of water decreased when salts were dissolved in it. In fact, Daniel Gabriel Fahrenheit used the freezing point of brine, or salt water, as his reference point for 0° on his now-famous temperature scale.

- In the modern era, tons of rock salt are spread onto icy roads and sidewalks in the United States alone to make travel safer by inducing melting. The use of rock salt relies on a phenomenon called freezing point depression.

- By interacting with the solvent through intermolecular forces, the salt ions interfere with the formation of the specific interactions between water molecules that are needed to form a solid. The result of this is a solution with a lower freezing point than usual.

- Dissolved solutes also have an effect on boiling points of solutions. Imagine a solution in which sodium and chloride ions are present near the surface. These nonvolatile solutes can't vaporize like water can, but they do occupy the solution near the surface, holding some of the solvent in a sphere of hydration, making it less likely to escape into the atmosphere and vaporize.

- The rule of thumb is that more concentrated solutions prefer to remain liquids. Their freezing points are depressed and their boiling points are elevated. The extent to which these phase transition temperatures change can be easily calculated if we know the constants governing those changes for the solvent in question. Those constants are called the molal freezing point depression constant and the molal boiling point depression constant.

- The freezing point depression that is experienced by any solution can be calculated using a generic equation: $\Delta T_f = i(-K_f)m$. This states that the change in freezing point (ΔT_f) is equal to the van't Hoff factor (i) times the freezing point depression constant ($-K_f$) that is unique to that particular solvent times the molality (m) of whatever it is that we've dissolved. The constant is negative to acknowledge that the freezing point is lowered.

- Boiling point elevations behave very similarly. The equation is very similar to the equation for freezing point depression, except this time we're focusing on the change in the boiling point temperature (ΔT_b) and we're using a new constant called the molal boiling point elevation constant (K_b), which is positive because the boiling point is elevated instead of lowered: $\Delta T_b = iK_b m$.

VAPOR PRESSURE

- If boiling point is elevated by the presence of solute, another way of saying this is that the vapor pressure of solutions is lower than that of the pure solvent at any given temperature. The vapor pressure of solutions is indeed reduced when nonvolatile solutes like sodium chloride are introduced.

- Just like boiling and freezing points, the change in vapor pressure is a simple function of concentration, although we have to use slightly different units of concentration to predict it.

- The vapor pressure of a solution will also change in response to the solution of a solute. The equation that we use for this is a little bit different. Instead of using molality, we rely on the mole fraction. But we're not using the mole fraction of the solute; we're using the mole fraction of the solvent. As that mole fraction decreases, so does the vapor pressure, which means that as concentration of the nonvolatile solute increases, so does the vapor pressure.

- The new vapor pressure exerted by a solution is equal to its mole fraction times the vapor pressure when the solvent is absolutely pure:

$$P_{\text{solution}} = \left(\frac{n_{\text{solvent}}}{n_{\text{solution}}}\right) P_{\text{solvent}}.$$

OSMOTIC PRESSURE

- The final property that depends only on the concentration of dissolved solute particles is osmotic pressure, which is most famous for its role in plant nutrient uptake. But osmotic pressure plays roles in many other biological processes.

- To understand how osmotic pressure works, consider just how small water molecules really are. Even as molecules and ions go, water molecules are among the tiniest around. So, it is possible—and nature does this quite often—to produce a membrane with pores so tiny that only water can get through. Any solutes dissolved in the water will be unable to pass.

- Now think about what you might expect to happen if you placed 2 solutions of different concentrations in the same container but separated them with such a membrane. Those 2 solutions really want to be of the same concentration to maximize the number of microstates that the system can have. But to accomplish this would mean mixing them. This can't happen because of the membrane.

- But there is something that the solution can do. Some of the water from the lower-concentration (or hypotonic) side can migrate across the membrane to the stronger (or hypertonic) side. When this happens, there is an imbalance in the masses on each side, which corresponds to a certain pressure.

- If we could push down on the more concentrated (or hypertonic) side hard enough to resist flow in from the less concentrated (or hypotonic) side, that is the osmotic pressure of a system. When one of the 2 solutions is pure water, it can be calculated using a simple equation: $\pi = iMRT$, where π is the osmotic pressure, M is molarity (which is equal to n/V), R is the ideal gas constant, and T is temperature. This equation is stunningly similar to the ideal gas law, but it still does contain a van't Hoff factor because it is a colligative property.

- Osmotic pressure is responsible for the rigidity of cell walls in plants, holding stems and leaves in place. Without it, the cells become pliable and wilting occurs.

- Different species of fish have evolved to cope with the varying salinity of oceans and freshwater lakes and streams. Oceanic species have to cope with the loss of water to their surroundings, which freshwater fish actually drink through their cell walls as the more dilute water around them works its way in. Switch their environments, and they both stand little chance of surviving.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 548–558.
Masterton and Hurley, *Chemistry*, 10.3–10.4.

QUESTIONS

1. Colligative properties are based on interactions between solute and solvent. With this in mind, do you expect these laws to be best obeyed in dilute solutions or more concentrated solutions?

2. At what temperature do you expect the following phase transitions to take place?

   a. Freezing of a 1.5-molal solution of sodium chloride

   b. Freezing of a 1.5-molal solution of magnesium chloride

   c. Boiling of a 1.5-molal solution of sucrose (sugar)

   d. Boiling of a 1.5-molal solution of potassium bromide

Answers
2a) 5.58°C; 2b)–8.37°C; 2c) 100.77°C; 2d) 101.54°C.

Modeling Reaction Rates

LECTURE 30

Most simply defined, rate is change over time. When we try to express a rate as a mathematical function, we express it as a change (Δ) in whatever we are interested in divided by a change in time (t). The rate at which chemical processes take place often are affected by the concentrations of the reacting materials. In this lecture, you will learn about reaction rates and rate laws.

RATE LAWS

› The rate of a given reaction is affected by the concentration of the reactants. But this leads to qualitative observations, while our goal is to understand how reaction rates are determined. To accomplish this goal, we use a reaction's rate law, which is an equation that relates concentration to rate.

› Let's consider the rate law for a generic reaction—one in which a moles of A reacts with b moles of B to form c moles of C and d moles of D: $aA + bB \rightarrow cC + dD$. We're going to use this reaction to estimate what its rate law is.

› Before we do that, we have to make some assumptions. Let's assume that this reaction doesn't go backward. In other words, as C and D accumulate, they do not affect the rate of the reaction at all. Let's also assume that this is an elementary reaction, meaning that it all happens in a single step. There is no complicated mechanism that goes on during the reaction; it's simply that a moles of A and b moles of B collide with one another, and a reaction takes place.

- If that's the case, we can get a rate law simply by looking at the reaction. The rate is proportional to the concentration of the reactants, A and B. Furthermore, we raise those concentrations to an exponent equal to their coefficients in an elementary reaction. In this case, that would be a and b.

- This is only a proportionality; it's not an equation yet. To make it an equation, we have to insert a proportionality constant, k. This is the rate constant, and the coefficients that have been brought in as exponents a and b become what we call a rate order.

$$\text{rate} = k(A)^a(B)^b$$

- When the rate expression contains an exponent of 1, this is called a first-order reaction. If instead we have an exponent of 2, this would be called a second-order reaction. It is possible to have multiple exponents, for example, when you have more than one reactant involved in the reaction. When that's the case, we add the exponents to create an overall order for the reaction.

- What if we're not certain that our reaction takes place in an elementary step? Or, even worse, what if we know that it doesn't? We can't use the coefficients from our reaction as our exponents. We have to determine them scientifically. If we want to know the rate order, we have to run the reaction under several conditions of concentration, measure the rates, and use that information to figure out exactly what the rate order is.

- As the order of a reaction changes, so does the rate constant units. Zero-order reactions will have rate constants of molar per second. First-order rate constants will have units of 1 over seconds, more often shown as reciprocal seconds, s^{-1}. A second-order reaction will have 1 over molar seconds, or $M^{-1}s^{-1}$, simply to be sure that everything cancels out in a way that gives us the appropriate units at the end.

INTEGRATED RATE LAWS

- Our discussion has led us to a point at which we can use a simple reaction's order and rate constant to predict a reaction's instantaneous rate at a given concentration. But there are other questions that we cannot yet answer. For example, if we start with a 1-molar solution of peroxide, how much peroxide will remain after 1 minute, or 1 hour?

- It gets a bit complicated. As peroxide reacts away, the concentration changes, and, therefore, so does the rate. The rate law itself can only tell us an instantaneous rate at one point in time, so it isn't quite ready to help us answer that question, but with a little bit of manipulation, it can be.

- We're going to apply some calculus to our understanding of chemical reaction rates and figure out a way to get different types of information than we can get using an original rate law that we derive.

- Let's consider this rate law: rate = $-kA^x$, where x is the order of the reaction with respect to the concentration of reagent A. The minus sign is included because we're considering this as the loss of a reactant; the minus sign lets us know that as time passes by, concentration of A will decrease, because it's a reactant.

- We can express the rate of this as dA/dt, the change in the concentration of reagent A as time changes. So, the equation becomes $dA/dt = -kA^x$. Let's multiply through by dt to cancel that and divide through by Ax, cancelling that.

- Now we have the equation $dA/A^x = -kdt$. This equality is ready for integration. If we consider 2 points—the initial time and then any time we'd like along the course of this reaction—we can create an integral to express that: the integral from 0 to t of the expression on the right and the integral from the initial concentration A_0 to the final concentration at that time A_t.

- The following is the generic form of an integrated rate law.

GENERAL

$$\boxed{\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^x} = \int_0^t -k\,dt}$$

- The order of the reaction with respect to A remains as x. If it happens to be a zero-order reaction, we simply place a 0 into the integrated rate law. If it's a first-order reaction, we use a 1, and if it's a second-order reaction, we use a 2, and so on. We can run the calculus on the following integral-based equations and create new rate laws that allow us to determine the concentration of reactants at any point in time along the reaction.

ZERO ORDER

$$\boxed{\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^{\mathbf{0}}} = \int_0^t -k\,dt} \quad \boxed{[A]_t - [A]_0 = -kt}$$

FIRST ORDER

$$\boxed{\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^{\mathbf{1}}} = \int_0^t -k\,dt} \quad \boxed{\ln[A]_t - \ln[A]_0 = -kt}$$

SECOND ORDER

$$\boxed{\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^{\mathbf{2}}} = \int_0^t -k\,dt} \quad \boxed{\left(\frac{1}{[A]_t}\right) - \left(\frac{1}{[A]_0}\right) = -kt}$$

- The integrated rate laws for reactions are even more powerful than the rate laws themselves, giving us an equation that can tell us exactly how much reagent should be consumed at any time whatsoever.

PROCESSES AND DATING

- Good or bad, it seems that change is inevitable as time passes. Molecules and atoms are not immune to the passage of time, either.

- In 1905, Ernest Rutherford and Bertram Boltwood were contemplating a way to exploit the fact that molecules and atoms change. At that time, Darwin had already published his famous *Origin of Species*, and geologists were beginning to posit the concept of supercontinents having existed in the distant past—a prologue to the theory of continental drift.

- Naturally, concepts like the evolution of species and continental drift raised some serious questions about the accepted age of the Earth. Was it old enough for these kinds of processes to have taken place? If so, how might we determine its age experimentally?

- Boltwood decided to tackle the issue using a very unusual clock—uranium atoms. Boltwood knew that uranium decayed radioactively, and thanks to the work of Rutherford, the rate at which uranium decayed was well characterized.

- Boltwood devised an experiment that allowed him to use the slow radioactive decay of uranium to estimate the age of minerals taken from the Earth. His new technique gave him the ability to measure the age of objects as ancient as the Earth itself.

- But let's step back and consider a simple example of how knowledge of rates can allow us to determine the age of an object that is older that we are. Imagine a process that begins long before you have the chance to observe it.

- Let's imagine that someone left the bathtub running and walked away. So, you enter the bathroom to find that the tub is quickly filling and has 50 gallons of water in it. How is that information useful? Let's also say that you know that the faucet dispenses water at 2 gallons per minute. Suddenly, you know that the culprit must have started this process 25 minutes ago.

- You figured this out by applying your knowledge of kinetics. The filling of the tub is a zero-order process; its rate does not change with time. So, you know the rate law governing the amount of water in the tub and the rate constant that completes the equation. After that, some simple math let you know that the process must have started 25 minutes earlier.

- Boltwood and Rutherford simply extended this kind of logic to the chemical world, where the decay and conversion of elements and molecules follow the same types of rate laws. So, knowing the rate order of a process and the rate constant for that process gives us a way to very accurately measure the age of closed systems, such as the mineral crystals in rocks and the cloth making up garments.

HALF-LIVES

- To really understand how chemical processes can act as clocks, we have to revisit our rate equations again. This time, we are looking for the best possible processes to use as chemical clocks. We want these processes to be predictable and reliable and to take place the same regardless of the conditions under which they began.

- The previous example of a zero-order process gave a nice illustration of how the rate of a process can be used to turn that process into a sort of clock that can tell us when the process started. We used a zero-order process—the filling of a bathtub—to illustrate how a constant rate process can work.

- The problem we usually run up against is that zero-order processes are rare in chemistry. Most naturally occurring decay processes, however, are first-order processes.

- At a glance, this might seem like a problem because first-order rates change as their starting materials are consumed. But the integrated rate laws uncover a very regular property of first-order decay processes that demonstrates how useful they can actually be for investigating.

- Enter Rutherford again. In 1909, he reported on a parameter that he called the half-life of a radioactive element.

FIRST ORDER HALF-LIVES

SPECIAL CONDITION FOR HALF-LIFE

$$\boxed{[A]_t = 0.5[A]_0}$$

FIRST ORDER INTEGRATED RATE LAW

$$\boxed{\ln[A]_t - \ln[A]_0 = -kt}$$

substitution using quotient rule of natural logarithms

$$\ln\frac{[A]_t}{[A]_0} = -kt$$

special designation ***$t_{1/2}$*** *for half-life*

$$\ln\frac{0.5[A]_0}{[A]_0} = -kt_{1/2}$$

$$\ln 0.5 = -kt_{1/2}$$

$$-0.693 = -kt_{1/2}$$

$$\frac{-0.693}{-k} = \frac{-kt_{1/2}}{-k}$$

HALF-LIFE FOR ANY FIRST-ORDER PROCESS

$$\boxed{\frac{0.693}{k} = t_{1/2}}$$

- First-order processes are particularly useful for dating because their half-lives are so consistent. It doesn't matter how much or how little of a particular material was present at the beginning. If it changes in a first-order process, it will do so with consistent and predictable half-lives. Common examples of this include uranium-238 and carbon-14, both elemental isotopes that decay.

- Now we can see the truly remarkable utility of radiometric dating. Because it uses a first-order process—that of radioactive decay—in theory it does not matter how much material is present when the clock starts. The half-life is always the same. In addition, the half-life itself represents the approximate timescale over which a particular dating method will be most useful.

- Imagine a sample of radioactive material isolated from its environment—for example, carbon-14 trapped in the cellulose of a growing tree or uranium-238 trapped in crystals of recently formed minerals. Those radioactive minerals slowly decay into what is called daughter products. Scientists can analyze the isolated sample for the amount of the parent isotope and the amount of its daughter products.

- The sum of the parent isotope plus the daughter products tips us off to how much of the parent isotope was originally in the trapped sample. Armed with this information, scientists can determine the original and final amounts of the parent isotope in the sample using the integrated first-order rate law or the first-order half-life equation.

- Uranium-238's half-life of 4.5 billion years makes it ideal for dating very early Earth processes, because on geologic timescales about half of a mineral sample's uranium-238 will decay into daughter products.

- Carbon-14, in contrast, has a half-life of 5740 years, making it perfect for dating artifacts from early civilizations made from organic materials like wood and bone. These materials contain trapped carbon atoms, just a few of which are carbon-14 and can be used to determine their age.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 576–593.
Masterton and Hurley, *Chemistry*, 11.1–11.3.

QUESTIONS

1 Do reaction rate orders need to necessarily be integer numbers, or is it possible for fractional rate orders to govern more complex processes?

2 Is it possible to use zero- or second-order reactions as dating methods? What additional information must be known to use such processes in this way?

3 In a given reaction, the doubling of the concentration of a reagent is observed to increase the reaction rate by a factor of 8. What is the order of the reaction with respect to this reagent?

Answer

3) third order ($2^3 = 8$).

Temperature and Reaction Rates

LECTURE 31

Cooling systems tends to lower their reaction rates, and heating systems tends to increase reaction rates. But why? Temperature is just increased molecular kinetic energy within any sample of matter. But what is it about increasing average molecular kinetic energy that would encourage a reaction to proceed with greater speed? And if we can understand this, then can we use that knowledge to bend nature to our will and engineer better devices and products that rely on chemical reactions? The answers to these questions are the topic of this lecture.

MOLECULAR COLLISIONS

- For chemical change to take place, atoms and molecules need to touch. But they need to come together with enough force to affect the desired chemical change.

- As the 20th century got underway, some of the heavyweights of physical chemistry, including future Nobel laureates van't Hoff and Arrhenius, were hard at work trying to piece together the code of how chemical change took place.

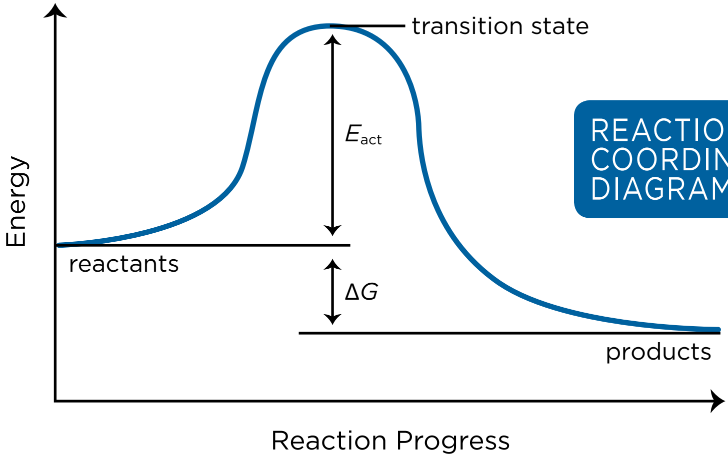
- By then, the nature of atoms and chemical bonds were fairly well pieced together, yet there was still an elusive question of exactly how one chemical substance changed into another. One of the more critical tools to figuring out this puzzle is careful measurement of reaction rates.

- But why does temperature affect a reaction? If atomic theory is correct, then the atoms and molecules that will react with one another in a chemical reaction must come into contact. Contact is critical, but it isn't necessarily enough. The contact has to happen with enough energy or the reactants simply bounce off one another and go on their way, unaltered.

- This necessary energy to initiate a chemical change is called a reaction's activation energy. Knowing the activation energy for a process is instrumental in designing chemical syntheses and modeling chemical reactions in ways that make our lives better, so we want to be able to measure and understand this critical parameter for any reaction that might be of interest.

REACTION COORDINATES

- To convert a material into a lower energy state first requires that we input some energy to initiate the process. We can show this concept graphically using a reaction coordinate diagram, which is a potential energy surface plotted as chemical potential energy on the *y*-axis and reaction progress on the *x*-axis.



REACTION COORDINATE DIAGRAM

- If we begin with a material of a certain energy and want to convert it into a material of a lower energy (a more stable material), we must first put some energy in. This makes the landscape for the system rise a bit first and then fall below the original energy, making it a spontaneous process.

- Consider a very simple reaction, such as 2 hydrogen atoms coming together to form a molecule of hydrogen gas. As the 2 atoms approach one another, the negatively charged surfaces of their electron clouds push against one another, resisting contact, so the system's chemical potential energy is increasing as they approach.

- If, however, the 2 come together with sufficient force to overcome that repulsion, they reach a distance at which their clouds overlap, forming a new covalent bond, which substantially reduces the energy of the system in the end, but only with some energy input at the beginning.

- The energy needed to traverse the energy barrier is called a reaction's activation energy, which is a crucial concept to understand because it directly impacts the rate at which a reaction takes place.

REACTIONS AND TEMPERATURE

- Temperature is just a way of reporting on the root-mean-square (rms) velocity of a group of particles. Some move faster than others, and some move slower, but the average velocity of a particle in a sample is related directly to temperature.

- Van't Hoff understood this relationship well and wondered if varying the temperature at which a given reaction took place would affect its rate predictably and consistently. He found that it did and that the relationship between temperature and reaction rate was not linear, but exponential.

- Van't Hoff was able to apply his intuition about molecular collisions and their effect on rates. His experiments proved that for a given reaction—such as the very simple hydrogen atoms to hydrogen gas reaction—increasing the temperature, and therefore the average kinetic energy, in a particle increased the frequency of collisions forceful enough to traverse the activation energy barrier for that reaction, ultimately manifesting itself as a faster reaction.

- As profound an observation as that was, van't Hoff's ideas raised even more questions than they answered. Can we formulate an equation that will allow us to determine the rate of any reaction? Can we use those formulas to learn something about the process of chemical change simply by observing the rate?

- The mantle of this question fell to Svante Arrhenius. Although van't Hoff paved the way with his measurements of rates and temperatures, it was Arrhenius who first suggested the concept of activation energy. Arrhenius got to thinking about molecular collisions and activation energies.

- Clearly, collisions had to happen with adequate energy and that energy could be provided by temperature increase. But can we measure that activation energy for a process? This was the question that burned for Arrhenius. To answer this question, he expanded on the work of van't Hoff and formulated what is known as the Arrhenius equation.

- We use the Arrhenius equation to mathematically relate the temperature to the rate of a given reaction. The following is one version of the Arrhenius equation: $k = Ae^{(-E_a/RT)}$.

- In this equation, the rate constant for any given process is a function of the Arrhenius constant (A), which is a collision factor that lets us know how many of the collisions that go on during a reaction are productive and actually start a reaction.

- We also have $e^{(-E_a/RT)}$, where E_a is the activation energy barrier for the reaction, R is the ideal gas constant in appropriate units, and T is the absolute temperature at which the reaction is being carried out. So, we have the influence of temperature on the rate of the reaction itself, but we have a few other things that we have to cope with before we can use the Arrhenius equation.

- We have the activation energy and the Arrhenius constant. We need to know what those are or at least how to deal with them before we can simply assess the effective temperature on rate. We can get started on doing that by thinking about how we can use this equation to determine the activation energy barrier for a reaction.

- We can rearrange this equation by taking the natural log of both sides. When we do that, we can use the rules of logarithms to get the $-E_a/RT$ term out of the exponent. The natural log of k is equal to the natural log of the Arrhenius constant minus E_a divided by R times T: $\ln k = \ln A - E_a/RT$.

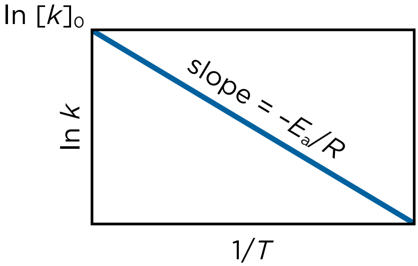
- If we think about this equation in a slightly rearranged form, it looks a bit like the equation for a line.

$$\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

$$y \;=\; m \qquad x \;+\; b$$

- What this means is that if we measure the rate constant as a function of the reciprocal of temperature, we can create a plot known as an Arrhenius plot, which gives us a way to access the activation energy for a reaction.

ARRHENIUS PLOT



- A few quick experiments measuring rates at various temperatures allows us to get the activation energy barrier that we're going to need if we're going to use the Arrhenius equation to make predictions about reactions in temperature.

APPLYING THE ARRHENIUS EQUATION

- The Arrhenius equation gives us a versatile tool to determine activation energies from rate data collected in the laboratory. Activation energies might seem a bit esoteric to the average person, a complicated physical constant relegated to the pages of manuals and reference books on the shelves of researchers or professors.

- But knowing the activation energy barrier for a process gives us real power—the power to predict relative rates at different temperatures. Although this might not sound like an important thing to be able to do, it becomes clear how powerful it is when we bring it to bear on a familiar topic: refrigeration.

- The Arrhenius equation, like practically all equations in chemistry, uses absolute temperature. So, the difference between room temperature of 25° centigrade and your refrigerator at 1° centigrade might seem large, but when we convert these temperatures to kelvin, we get 298 and 274 kelvin. That is just an 8% reduction in absolute temperature.

- It is the temperature term in the exponential of this equation that allows us to explain why refrigeration is so effective at food preservation.

- The following equation relates the relative rates of a reaction at 2 different temperatures based on the activation energy barrier, but not the Arrhenius constant. This simplifies things dramatically.

$$\ln\frac{k_1}{k_2}=\left(\frac{E_a}{R}\right)\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

- Knowing the activation energy for common food spoilage reactions and the Arrhenius equation allows us to show why we bother lowering the absolute temperature of storage for certain foods by only about 10%. It is because the Arrhenius equation shows that rate is exponentially related to temperature and what may seem like a slight temperature change can actually have large effects on reaction rates.

- Arrhenius's work also extends to the biological world, where organisms known as cryophiles can thrive in temperatures as low as −20°C, or −4°F. Conversely, organisms known as thermophiles have been found growing in temperatures as high as 122°C or 251°F, such as hot springs in Yellowstone National Park and geothermal vents on the seafloor.

- These cold- and hot-loving organisms, collectively called extremophiles, have found a great niche in their biospace. There isn't much competition for resources inside of a glacier or superheated seawater. But to lay claim to these hostile regions, they have had to alter their biochemistry drastically to cope with the different rates of reactions that keep them alive.

- When scientist break them down, extremophiles often are found to have remarkably exotic enzymes, cell wall structures, and other features that help them endure those locations.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 593–599.
Masterton and Hurley, *Chemistry*, 11.4–11.5.

QUESTIONS

1. According to the Arrhenius equation, is it ever possible for a given reaction to run more slowly at a higher temperature?

2. The Arrhenius factor corrects for the force with which molecules must collide for a simple reaction to take place. Are there any other factors to consider that might affect the Arrhenius factor for a given reaction?

Reaction Mechanisms and Catalysis

LECTURE 32

Chemical reactions are rarely a single, concerted process—a direct transition from reactants to products—but rather often consist of several or many conversions in sequence, all of which add up to a more complex process in which the reagents ultimately become products but sample other states along the way. These states are called intermediates, and they are unique from starting materials and products because they both form and are consumed in the reaction. In this lecture, you will consider chemical reactions and how rates can help uncover their mechanisms.

REACTION MECHANISMS AND ELEMENTARY STEPS

› Most of the reactions that we have considered so far have been oversimplified. Our early discussions about rate laws required that we assume that reactions take place in a single concerted step, meaning that the conversion from reactants to products happens directly, all at once, in a single collision of reactants. But the truth about chemical change is that it is rarely so simple.

› Just think about it from a probability standpoint. We sometimes classify reactions based on the number of molecules that must participate for a reaction to take place. When just one molecule reacts, that reaction is called unimolecular, 2 would be called a bimolecular reaction, 3 molecules of reactants makes for a trimolecular reaction, and so on.

- Reactions involving a single molecule can happen at any time, with no collision needed, but bonds must be vibrating, twisting, or in some other way moving just right to kick off the reaction. There is no problem there, because bonds are always doing this at all temperatures but absolute zero.

- A bimolecular reaction would require that 2 molecules find each other, collide in just the right orientation, and do so with just the right amount of energy to promote the process. This is a bit less likely.

- But imagine even more complex reactions with greater numbers of reactants, such as most combustion reactions. If methanol combustion were an elementary reaction, 3 molecules—2 of oxygen and one of methanol—would have to collide simultaneously, all in the proper orientation and with enough energy for a reaction to take place. The combustion of ethanol would require that 4 molecules do so.

- The likelihood of such a confluence of collisions would be so rare that such a reaction would not happen at all. However, we know that these reactions happen. In fact, they happen quite vigorously when the reagents are combined in the proper proportions, and a small spark sets them off by providing the initial activation energy. So, these processes have to happen differently.

- What if, instead of colliding all at once, the reaction took place in a stepwise fashion? What if a molecule of oxygen reacts with methanol, forming something different—an intermediate? This intermediate could then react with another oxygen in a second simple step.

- To better understand reactions and how to manipulate them, we need to understand exactly what is happening at the level of chemical bonds. Which bonds break and form and in what order?

- Reactions often happen in a stepwise fashion, and different steps each take place at their own rates. Through a process of sequentially breaking and forming bonds, the materials reacting transition from one species to another, then another, until the final product is formed.

- Some changes take place very early in the process, and some take place much later. Some happen rapidly, and others much more slowly, and all of the individual steps play an important role in the completion of a reaction.

- Multistep mechanisms are critical to understand. But how do we decipher this puzzle? How is it possible to determine the mechanism, or set of elementary steps, that converts one material to another when they are all going on in concert over a vast sample of moles of molecules inside of a reaction mixture on the lab bench?

- At a glance, this seems like a puzzle that is impossible to solve. Without the ability to simply watch a handful of chemicals react, how can we possibly acquire this knowledge? The answer to this question comes from chemical kinetics—the very rate laws that we are studying in this segment of the course.

- In the case of elementary reactions, rate laws are relatively straightforward to determine. The order of the reaction is equal to the molecularity of the reaction. In other words, an elementary reaction involving a single reactant will always be first order in that reactant. An elementary reaction involving 2 reactant molecules will always be second order overall.

- But when we begin to consider processes that happen in a stepwise fashion, things change. The speed of the process is dictated by the speed of the slowest step in the process. The slowest step in a process is called the rate-determining step for that process, sometimes also called the rate-limiting step.

- The rate-limiting step will be the determining factor in the speed of the overall chemical reaction process. The speed with which we reach the rate-limiting step has something to do with how fast we get there, but once we pass this slowest step in the process, the effect of all of the subsequent steps we go through becomes negligible.

- By carefully considering all reasonable mechanisms and rate data for a given reaction, chemists can often come to a realistic understanding of how molecules interchange even in some of the most complex processes.

RATE LAWS

OVERALL REACTION

$1A + 1B \longrightarrow \text{products}$ rate = $k[A]^1[B]^1$

GENERIC MULTISTEP MECHANISM

VERSION 1 (FAST STEP FIRST)

$1A \longrightarrow 1X + 1B \longrightarrow \text{products}$

step 1 (**fast**)	$1A \longrightarrow \cancel{1X}$	rate = $k_1[A]^1$
step 2 (**slow**)	$\cancel{1X} + 1B \longrightarrow \text{products}$	rate = $k_2[B]^1[X]^1$
overall	$1A + 1B \longrightarrow \text{products}$	rate = $k_{\text{rxn}}[A]^1[B]^1$

$\boxed{k_{\text{rxn}} = k_1 \times k_2}$

VERSION 2 (SLOW STEP FIRST)

$1A \longrightarrow 1X + 1B \longrightarrow \text{products}$

step 1 (**slow**)	$1A \longrightarrow \cancel{1X}$	rate = $k_1[A]^1$
step 2 (**fast**)	$\cancel{1X} + 1B \longrightarrow \text{products}$	rate = $k_2[B]^1[X]^1$

Only consider the first step because it is the rate-limiting step.

overall	$1A + 1B \longrightarrow \text{products}$	rate = $k_{\text{rxn}}[A]$

$\boxed{k_{\text{rxn}} = k_1}$

CATALYSIS

- We have considered materials that are consumed in reactions (reactants), materials that are formed (products), and materials that form early but are later consumed in multistep reactions. There is one last permutation that we have not yet considered: a material that is present at the start of a reaction, consumed in an early step in the reaction, but is also produced in a subsequent step.

- The presence of this special material can sometimes alter the mechanism of a reaction drastically. Sometimes, such a species can take a reaction mechanism down a new road—one that requires less activation energy and can happen faster.

- When the addition of a material speeds a reaction without consuming that material itself, the process is called catalysis and the chemical that speeds the reaction without being consumed is called a catalyst. Jöns Jakob Berzelius coined this term in 1835, using a Greek word meaning "pick up" or "dissolve" as the root for his new discovery.

- Catalysis is a remarkable thing—not only because of how useful it can be to have control over the speed of a reaction for scientific study and demonstration, but also because of how commonly we see it even in nature.

- Berzelius noticed that certain noble metals like platinum speed certain reactions involving hydrogen gas, a fact used in food-processing plants around the world today, where platinum and other metals like it are used to speed the process of adding hydrogen to vegetable oils to form partially hydrogenated oils that have a longer shelf life.

- This class of catalyst is called a heterogeneous catalyst because it involves multiple phases. Alternatively, a homogeneous catalyst involves the catalyst being in the same phase as the reactants. Heterogeneous catalysis requires a bit more engineering, because heterogeneous catalysts, such as a solid platinum surface, provide a catalytic surface on which liquid and gas materials can bind to the surface, or adsorb, where they react, and then form products, which then desorb from the surface, making room for more reactant to adsorb and repeat the process. This means that more surface area means a more effective catalyst.

- Your car's catalytic converter uses a heterogenous catalyst of platinum and rhodium to modify the gas exhaust of your vehicle. Because of this, the catalyst itself is molded into a honeycomb-like structure to maximize the amount of exposed surface area. This minimizes the amount of these precious metals needed to carry out catalysis, which is a good thing, because platinum and rhodium are both much more expensive than gold.

BIOLOGICAL CATALYSTS

- The amazing influence of catalysts on our lives doesn't stop with noble metals like platinum. In fact, some of the most powerful catalysts are at work inside our bodies.

- The idea of biological catalysts was championed by Eduard Buchner, who found in 1897 that the extract of yeast cells known to carry out fermentation could carry out the process even when no living yeast were present.

- This observation forever changed the way that chemists look at living organisms. It made them realize that life itself is a composite of thousands of chemical reactions, each of which is moderated by special catalysts that our body manufactures to keep everything running smoothly.

- These special biological catalysts are called enzymes. These enzymes are designed to speed an array of chemical reactions that keep you alive. From phosphorylating adenosine diphosphate (ADP) to help you manage energy, to breaking down unwanted molecules in your bloodstream to prepare them for removal, to repairing chemically damaged DNA, enzymes are truly the caretakers of your body's chemistry.

- You might think of enzymes as manufacturing equipment on an assembly line. The equipment is all designed to speed the conversion of parts into products, all while maintaining its own integrity so that it can be used again and again to efficiently promote the desired process. It participates in the process, but is not consumed.

- But what is really stunning is the kind of rate acceleration that enzymes can achieve for certain reactions. Enzymes can speed many reactions by a factor of a million, a billion, or a trillion times, and sometimes even more.

- This incredible catalytic power has led to enzymes being used in a variety of commercial products, such as detergents, where they catalyze the chemical breakdown of proteins and fats to remove stains.

- The ability of enzymes to accelerate very specific reactions by tremendous factors is unrivaled by any other catalyst known. Without them, the complex chemical symphony going on within our bodies would be impossible. The human race itself owes its very existence to this class of catalysts.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 599–615.
Masterton and Hurley, *Chemistry*, 11.6–11.7.

QUESTIONS

1 Is it necessary for a catalyst to participate in a step prior to the rate-limiting step in a reaction mechanism to be effective at increasing the overall reaction rate?

2 Consider the following reaction mechanism:

Step 1: $F_{2\,(g)} + NO_{2\,(g)} \rightarrow FNO_{2\,(g)} + F_{(g)}$

Step 2: $F_{(g)} + NO_{2\,(g)} \rightarrow FNO_{2\,(g)}$

If the rate law for the overall reaction is experimentally determined to be rate = $k[F_2][NO_2]$, which step of the proposed mechanism must be rate limiting? What is the rate law expected to be if the other step is in fact limiting?

Answer

2) The first step is rate limiting. If the second step were rate limiting, the rate law would be rate = $k[F_2][NO_2]^2$.

The Back and Forth of Equilibrium

LECTURE 33

An equilibrium is a dynamic state in which change is still taking place—forward and backward—but at identical rates. One common misconception is that equilibrium means that there are equal amounts of starting material and product. This is not always true; in fact, it is rarely true. It is possible for populations of chemical reactants and products to be different even when the forward and reverse rates are the same. Systems at or on their way to establishing equilibrium follow a remarkably simple mathematical model. By the end of this lecture, you will be well on your way to understanding the equations that govern this critical chemical process.

HOMOGENEOUS AND HETEROGENEOUS EQUILIBRIA

- Chemical equilibria fall into 2 general classes. The first of these classes is homogeneous equilibria. In homogeneous equilibria, all of the reactants and products of the process are of the same phase. For example, the synthesis of gas-phase methanol from the gases carbon monoxide and hydrogen would fall into this class, because all 3 species—the 2 reactants and the product—are all in the gas phase.

- The second class is heterogeneous equilibria. In heterogeneous equilibria, reactants and products of differing phases are being interconverted. For example, the combustion of carbon using oxygen, a reaction constantly going on in power plants and barbeque grills around the world, is a heterogeneous equilibrium, where solid carbon reacts with gaseous oxygen to form gaseous carbon dioxide.

- In this lecture, we will focus on homogeneous equilibria in the gas phase. Once we have learned the tools necessary to investigate, model, and even manipulate this class of equilibrium, we will return to the others and see how they fit in.

THE EQUILIBRIUM CONSTANT

- We have defined equilibrium as a state in which forward and reverse reaction rates are equal to one another. This is good news, because it means that there must be some connection between rate laws and how systems behave at equilibrium.

- Our goal is to consider reactions not just in a unidirectional sense, but in the sense that they can sometimes go backward. The reaction of NO_2 to form N_2O_4 is an example. We have seen reactions like this quite a few times and have always presumed that whichever direction we wrote the reaction in was the only direction it could go—meaning that 2 NO_2 molecules can form N_2O_4 but can't go back the other direction.

- This reaction would be governed by a rate law that would be *k* for that reaction times the concentration of $(NO_2)^2$, assuming that this is an elementary reaction: $\text{rate}_{\text{fwd}} = k_{\text{fwd}}(NO_2)^2$.

- Let's now consider the possibility that this reaction could go in reverse—that N_2O_4 might decompose and form NO_2 molecules. If that were to happen, we would have a rate law that would be $\text{rate}_{\text{rev}} = k_{\text{rev}}(N_2O_4)$, which uses a different *k* value, one for the reverse reaction, times the concentration of N_2O_4, the product.

$$2\ NO_{2\ (g)} \xrightleftharpoons[\text{rate}_{\text{rev}} = k_{\text{rev}}[N_2O_4]]{\text{rate}_{\text{fwd}} = k_{\text{fwd}}[NO_2]^2} N_2O_{4\ (g)}$$

- The central idea around equilibrium is that reactions can go forward and backward and establish a situation in which rates are equal. If rates must be equal for equilibrium to have been established, that means that in this case, the forward rate law expression must be equal to the reverse rate law expression.

- Doing a little bit of rearranging—dividing through by the reverse rate constant and again by the concentration of $(NO_2)^2$—gives us a new relationship, where k for the forward reaction divided by k for the reverse reaction is equal to the concentration of products raised to an exponent equal to their coefficient divided by the concentration of starting material raised to a power of their coefficient. This relationship, k_{fwd}/k_{rev}, is called K, the equilibrium constant for our reaction.

SPECIAL CONDITION FOR EQUILIBRIUM

$$\boxed{rate_{fwd} = rate_{rev}}$$

$$\frac{k_{fwd}[NO_2]^2}{k_{rev}[NO_2]^2} = \frac{k_{rev}[N_2O_4]}{k_{rev}[NO_2]^2} = K_{eq}$$

- Let's think about how to derive the equilibrium constant in a simpler way now that we understand the inner workings. The following is a reaction that is also an equilibrium: 3 moles of oxygen gas (O_2) in equilibrium with 2 moles of ozone gas (O_3). We don't know for sure that this will be the equilibrium concentrations, but it is the stoichiometry of the reaction. That means that oxygen can react to form ozone.

- We now know that we have to consider that ozone can also react with itself to form oxygen. The process can be reversed. The equilibrium is governed by the equilibrium constant in which we have the products raised to their coefficients over the reactants raised to their coefficients.

- In this very simple case, we have a situation where the equilibrium is $(O_3)^2/(O_2)^3$. Ozone is in the numerator because it is a product, and it is raised to a power of 2 because of its coefficient, and oxygen is in the denominator because it's a reactant, and it is raised to a power of 3 because of its coefficient. This is the expression for the equilibrium constant.

$$3\ O_{2\,(g)} \rightleftharpoons 2\ O_{3\,(g)}$$

$$K_{eq} = \frac{[\text{products}]^{\text{coefficient}}}{[\text{reactants}]^{\text{coefficient}}} = \frac{[O_3]^2}{[O_2]^3}$$

- The predetermined equilibrium constant allows us to sit at our desk and answer questions about experiments that we haven't run yet. Just think of all the time and cost and trouble that we can save, all because we understand how the equilibrium constant works.

FACTORS AFFECTING K_{eq}

- Because it is derived from a written equilibrium reaction, the value of K for any reaction can depend on certain choices about how we write the reaction.

- For example, consider the reaction $1\ H_2 + 1\ I_2 \rightleftharpoons 2\ HI$. We can also write this reaction as $\frac{1}{2}\ H_2 + \frac{1}{2}\ I_2 \rightleftharpoons 1\ HI$. If we do that, and use this reaction instead to determine K_{eq}, the exponents in K_{eq} will be half those of the original expression. This means that if we chose to write the reaction this way, effectively halving the reaction, we would have to use the square root of the value K that we determine from the original expression.

- Also, consider that if we reverse the reaction, making products reactants and vice versa, forming 1 mole of H_2 and 1 mole of I_2 from 2 moles of HI, the rate constant becomes inverted. We have to compensate for that by using the reciprocal of K_{eq} as we calculate it originally.

- It is critical to carefully consider how a reaction is written in your problem and make sure that it is consistent with the K_{eq} value that you are using to solve problems.

REACTION QUOTIENTS

- When a nonequilibrium mixture of reagents is created, we sometimes want to know which direction that equilibrium will shift without necessarily needing to know exactly how much of each component will be consumed or produced.

- When this is the case, we can use a mathematical tool called a reaction quotient to get a quick read on roughly how far a mixture is from equilibrium and which way it will shift to get there.

- The equilibrium constant expression for any equilibrium will be some function of products divided by some function of reactants. Essentially, their concentrations are raised to a power equal to their coefficients.

- What if we were to use the equilibrium constant expression to describe a system that's not at equilibrium? It wouldn't be the equilibrium constant anymore; it would be something else, and that something else is called Q, or the reaction quotient.

- We can still put concentrations of products and reactants into the expression; they're just not necessarily equilibrium concentrations anymore. This will give us a tool that we can use to predict how equilibrium will shift or a how a system will shift to reach equilibrium.

$$aA + bB \rightleftharpoons cC + dD$$

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Let's say that we have a system and we calculate Q and determine that it's exactly equal to the equilibrium constant. What does that tell us about the system? It tells us that we're at equilibrium. This is going to be a very boring reaction, because nothing's going to change.

- If we put initial concentrations into the expression for Q and find that it's actually less than the equilibrium constant, that tells us something very valuable. If Q is smaller than K_{eq}, that means that its number is smaller, which means that its numerator is smaller, or its denominator is too large to be equal to K itself.

- What will a chemical system do to rectify this problem and get Q equal to K? It's going to move to the right toward the products, bringing other concentrations up (increasing the numerator) and bringing reactant concentrations down (shrinking the denominator), until Q is equal to K again. When Q is smaller than K, the equilibrium will shift to the right, toward the products.

- Similarly, what if we find that Q is greater than K? The concentrations tell us that the number is too large when you put it into the equilibrium constant expression. That would be a situation in which the products are too big (the numerator is too large) and the reactants are too small (the denominator is too small), creating a very large value for Q.

- What can the reaction do to remedy this problem? It can go backward; it is an equilibrium. It can decrease products and increase reactants until it's back where it belongs, at equilibrium. Q, the reaction quotient, gives us a valuable tool to determine which direction a system will shift to reach equilibrium.

- If Q is equal to K, we're at equilibrium, and there is no shift. If Q is greater than K, the system will shift to the left, toward whatever we've defined as the starting materials, or reactants. If Q is less than K, we expect the system to shift to the right, creating more of what we've defined as products and consuming more reactants.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 629–649.
Masterton and Hurley, *Chemistry*, 12.1–12.4.

QUESTIONS

1 Equilibrium applies to all processes, not just chemical processes. What are some equilibrium processes that are taking place around you right now?

2 Heating and cooling can sometimes cause equilibria to shift by stabilizing or destabilizing reactants and products. Is this effect a result of the changing equilibrium constant (K) or reaction quotient (Q)?

Answer

2) Heating a system affects the reaction constant K (recall that Q depends only on concentrations of reactants and products).

Manipulating Chemical Equilibrium

LECTURE 34

The temperature and pressure conditions under which reactions take place can be changed. When they are changed, the equilibrium constant for a reaction can also change, causing a shift in the equilibrium that allows us to, at least partially, bend an equilibrium to our will. In this lecture, you will learn about 3 ways that gas-phase equilibria can be altered using Le Chatelier's principle—by manipulating concentration, temperature, and pressure.

LE CHATELIER'S PRINCIPLE

- Claude-Louis Berthollet was the first to give serious thought to the notion that reactions might run in reverse, creating dynamic equilibria for certain reactions. This changed our way of thinking about how matter interconverts, forcing us to consider the possibility of equilibria in chemical reactions.

- But the real inspiration for how to manipulate equilibrium processes would have to wait 2 more generations for a man named Henry-Louis Le Chatelier, who would ultimately help us unify Gibbs's ideas about free energy with Berthollet's brainchild of chemical equilibrium.

- Le Chatelier, being classically trained in France, was no stranger to the concept of chemical equilibrium, as it had been advanced by Berthollet nearly a century earlier. In fact, Le Chatelier's father was influential in the development of the French aluminum, iron, and steel industries, so it probably came as little surprise when a young Henry-Louis expressed an interest in chemistry.

- It also might explain his acute interest in the effects of temperature on reactions. This might invoke images of Svante Arrhenius, who is commonly credited with linking temperature and reaction rates for irreversible processes.

- But what distinguishes Le Chatelier's work from Arrhenius's is that Le Chatelier was interested in the effect of temperature on equilibria. His study of equilibria under varying conditions led him to a conclusion that is known as Le Chatelier's principle: A chemical system placed under a stress will shift in a manner that relieves that stress.

- Chemicals don't like to be stressed any more than you do. If we alter the conditions surrounding a particular chemical system—whether they are concentrations, temperatures, or pressures—the system will try to undo our changes by undergoing a shift in its equilibrium. How can such a simple observation open the door to bending equilibria to our will?

CONCENTRATION AND EQUILIBRIUM

- Concentrations of both reactants and products can dictate the direction that a system will shift to reach equilibrium. This can be illustrated using the reaction quotient. Starting with very high reactant concentrations tends to make smaller reaction quotients, ensuring that the system will shift toward products. And starting with relatively high product concentrations would cause the reaction to run in reverse to establish equilibrium.

- Imagine a system already at equilibrium. What happens if we disturb this equilibrium by the addition or removal of products and reactants?

- The effect of changing concentrations on a reaction's equilibrium can be best demonstrated using reaction quotients and equilibrium constants. Consider the reaction of NO_2 in equilibrium with N_2O_4. Let's assume that we are going to change the concentrations.

- Let's pretend that the following is the equilibrium mixture. We know that the equilibrium constant is not equal to 1, but that's sort of what we made it look like, or at least very close to it, just for the purpose of demonstrating the principle.

$$2\ NO_{2\,(g)} \rightleftharpoons N_2O_{4\,(g)}$$

$$K_{eq} = \frac{[N_2O_4]}{[NO_2]^2} \qquad Q = \frac{[N_2O_4]}{[NO_2]^2}$$

- We've defined N_2O_4 as the product and NO_2 as the starting material in the equilibrium. They are confined within a certain space.

- There is an equilibrium constant that governs this equilibrium. We're not sure what it is at this point because we don't know the temperature. Let's just say that it is K_{eq}, and we also have Q, the reaction quotient.

- If the system is at equilibrium, then there shouldn't be any shift. But let's put the system under stress by adding extra NO_2, increasing its concentration, and therefore increasing the value of Q.

- Now the system is going to abide by Le Chatelier's principle and try to find a way to relieve the stress that we just created—the increase in the concentration of NO_2. To fix that problem, what can the reaction do? How can this reaction decrease the concentration of NO_2?

- The reaction can shift: The equilibrium can move in favor of N_2O_4, bringing Q back in line with the ratio that we expect from the equilibrium constant, K. In other words, the system must shift to make Q equal to K.

- This is an explanation of how and why concentration can be used to manipulate equilibria and maximize the amount of whatever reactant or product we want to be present in the system.

TEMPERATURE AND EQUILIBRIUM

- Let's start our next inquiry where Le Chatelier did. The son of a materials engineer with great accomplishments in the processing of metals, Henry-Louis unsurprisingly took an interest in high-temperature chemistry.

- The key to understanding how Le Chatelier's principle applies to temperature is to think of heat as a product or reactant in a chemical process, just like any other reactant or product made of matter.

- Reactions can either generate or consume heat as they progress. Those reactions that consume heat from their surroundings are called endothermic, while those that release heat into their surroundings are exothermic.

- The symbol ΔH is used to indicate the flow of heat during a reaction. When ΔH is positive, the reaction is endothermic, consuming heat as it progresses. When ΔH is negative, the reaction is exothermic, releasing heat.

- Let's return to our reaction of NO_2 and N_2O_4 and think about how temperature affects equilibrium. The reaction is written as an exothermic process. The conversion of 2 moles of NO_2 into a mole of N_2O_4 releases 57.2 kilojoules per mole of heat.

$$2\ NO_{2\,(g)} \rightleftarrows N_2O_{4\,(g)}$$

$$\boxed{+\ \mathbf{HEAT}}$$

$$\Delta H = -57.2\ \text{kJ/mol}$$

- This means that we can think of heat as though it were a product of the reaction. Instead of showing the reaction that way, let's instead think of it as generically being a reaction in which heat is a product. That gets us more in line with thinking about Le Chatelier's principle.

- When you increase or decrease the concentration of a product, you shift an equilibrium. This time it's not a physical product; instead, we're thinking about heat. The system can fight any temperature changes that we try to make by pushing the equilibrium one way or the other—specifically, when NO_2 comes together to make N_2O_4, it releases a certain amount of heat into the system.

- If the system is at equilibrium and we cool it down, then Le Chatelier's principle says that reaction is not in equilibrium anymore. When we take some heat away, the system is going to try to undo our work by producing heat. This is accomplished by shifting the equilibrium in the direction of N_2O_4. By making a new molecule of N_2O_4 in the system, it heats up again.

- If we continue to try to cool this system down, the system will continue to battle us, making more and more N_2O_4. We can control this reaction simply by modulating the temperature.

- If instead it were our goal to make more of the NO_2, we would raise the temperature of the reaction. Le Chatelier's principle again predicts that the system will fight us and go in the other direction. Altering temperature in this case is not that much different than altering the concentration of the product or reactant. It still abides by Le Chatelier's principle.

PRESSURE AND EQUILIBRIUM

- Temperature can push reactions backward and forward, particularly when there is a large change in enthalpy between reactants and products. But temperature isn't the only condition that can matter. Another way that we can stress gas-phase reactions like NO_2-N_2O_4 equilibrium is with pressure.

- Pressure is generated by the collisions of gas particles with the walls of their container. More frequent collisions mean more pressure. So, if we increase the pressure on a system of gases like NO_2 and N_2O_4, and Le Chatelier's principle applies, how might this system shift to undo the pressure change?

- Pressure is related to several things, not the least of which is the number of moles of gas that are present. Remember the ideal gas law: $PV = nRT$. In this case, we have a reaction in which 2 moles of gas (NO_2) as the starting material are in equilibrium with 1 mole of gas (N_2O_4) as the product. This system can change the number of moles of gas present by shifting.

- If we were to squeeze this system down, we would increase the pressure that it's under, simply by changing the volume. When we force the volume down, the pressure of the system is naturally going to increase, because of the gas laws. Le Chatelier's principle says this system is going to sense that increase in pressure and immediately try to take steps to undo what we have done.

- The temperature is constant, but we're increasing the pressure. What can this reaction do to undo this work? It can change the number of moles. The ideal gas law contains a term for number of moles. We are controlling the volume and the temperature, but the reaction has control over how many moles of each gas are present.

- To reduce that pressure, the reaction can reduce the number of moles present by reacting, forming N_2O_4. Fewer moles of gas mean a lower pressure. Through Le Chatelier's principle, the system has partially undone the work that we just did.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 649–658.
Hager, *The Alchemy of Air*.
Masterton and Hurley, *Chemistry*, 12.5.

QUESTIONS

1 In the unusual case that a reaction has no net enthalpy or entropy change, is heating or cooling expected to alter the equilibrium in any way? If so, how?

2 According to Le Chatelier's principle and the equations studied in the past 2 lectures, is it ever possible for a system to completely relieve an applied stress?

Acids, Bases, and the pH Scale

LECTURE 35

Acids and bases have remarkable chemical power. They are largely responsible for the weathering of certain types of rock in the environment, are common ingredients in the foods you eat every day, and even help keep your body's chemistry running smoothly. What is so remarkable about acids—beyond their influence in nature, medicine, and engineering—is that they exercise this influence using some of the smallest ions that the universe has to offer. This lecture is dedicated to beginning to understand what is meant by the terms "acid" and "base" and why so much confusion exists around their effects on people and our environment.

DEFINING ACIDS AND BASES

› Although there are multiple ways to categorize acids and bases, we're going to focus on just 2 of those ways. In the Arrhenius definition, an acid is simply anything that can break apart or ionize to form an $H+$ in some kind of additional molecule or ion that it leaves behind. Examples of this would include HCL, which provides protons and chloride ions, or nitric acid, which comes apart to form protons and nitrate ions.

› Under the Arrhenius definition, a base is anything that dissociates in solution to form hydroxide ions ($OH-$). If a molecule directly dissociates to form $OH-$, it can be considered an Arrhenius base. A classic example of this are the components of lye, sodium hydroxide and potassium hydroxide, which dissociate to form $OH-$.

- Because there are a number of materials that, when added to water, have basic properties but don't actually carry hydroxide ions themselves, we're going to switch to a different definition for the rest of this lecture. We're going to discuss Brønsted-Lowry bases and acids.

- In the Brønsted-Lowry definition, an acid is defined in exactly the same way that it is in the Arrhenius definition. It has to be something that releases a proton. HCL and HNO_3 are perfect examples of Brønsted-Lowry acids.

- A Brønsted-Lowry base is a little different. A Brønsted-Lowry base is a proton acceptor. It's some type of molecule or ion that, when in the presence of protons, will bond to the proton, scavenging it from solution.

- A Brønsted-Lowry base, when added to water, will take a proton away from the water, and the result is that it leaves behind the balance, which is hydroxide ions. Even though they don't have hydroxide ions directly attached to them, Brønsted-Lowry bases can create them via the water that they're being dissolved in. Examples of this include carbonate ions, which take a proton to form bicarbonate and hydroxide, and ammonia, which reacts with water to form ammonium ion and the hydroxide that makes it basic.

- Ammonia is well known to create basic solutions when dissolved in water. Dissolving NH_3 in water produces $OH-$ ions like a base. The problem is that ammonia contains no oxygen. This exposes a serious flaw in the Arrhenius definition of bases. How can ammonia produce hydroxide ions? It doesn't have the right elemental makeup.

- It is a flaw that did not go undetected in the scientific community, and it did not take long for 2 researchers to independently modify the Arrhenius definition of a base to account for this observation.

- Arrhenius failed to consider the solvent in his acid-base theory. He simply assumed that water was an inert substance, only there to solvate ions provided by the acid or base itself as it ionized. In that respect, Arrhenius could not have been more wrong.

- In 1923, Johannes Nicolaus Brønsted and Thomas Martin Lowry each independently proposed that Arrhenius's definition of a base had to be modified. They both proposed that bases be defined not as hydroxide donors, but as proton acceptors—compounds that can bond to protons and remove them from solution.

- According to the Brønsted-Lowry theory, acids and bases are locked in a chemical dance, one releasing protons into solution and the other scavenging them. This concept applies to acid-base chemistry.

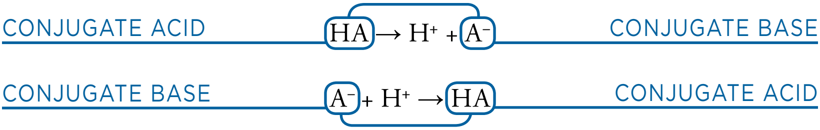
- Any time an acid releases a proton, it dissociates to produce not just protons, but a second piece of that acid, which is essentially the acid minus a proton. When a base picks up a proton, naturally it creates a new material that is itself plus a proton.

- These processes are the reverse of one another. So, for any acid dissociation or base association, we can simply reverse the process, and each starts to look a lot like its alter ego—acid dissociation reactions like base association reactions and base association reactions like acid dissociation reactions.

- Clearly, there is a special relationship between acids and the material that they become when deprived of a proton. Similarly, a relationship exists between bases and their association reaction product with an extra proton.

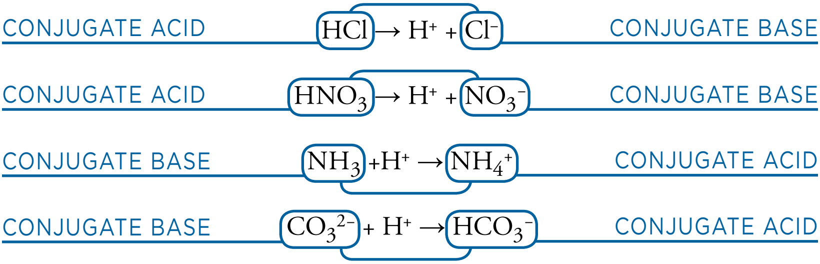
CONJUGATE ACIDS AND BASES

- One of the special relationships that acids and bases share with each other is the conjugate acid-base relationship. In a generic formula, a Brønsted-Lowry acid is any compound HA that dissociates to form protons and something else—in this case, an A– ion. The reverse of that reaction is a Brønsted-Lowry base. A– picking up a proton would cause HA to form. HA and A– are called conjugate acids and bases of one another.



- To be a conjugate acid or base is to be a part of a pair. It's not an absolute term. So, HA is not a conjugate acid in general—it's a conjugate acid of A–.

- The easiest way to identify conjugate bases and acids is to simply look for a difference of an H+, one proton and one unit of charge. When you see 2 species that differ only by a proton, they are by definition conjugate acids and bases.



THE pH SCALE

- The simplest class of Brønsted-Lowry acids are called strong acids. Those are hydrochloric, hydrobromic, hydroiodic, nitric, sulfuric, and perchloric acids. These acids have exceedingly weak bonds to their acidic hydrogens and will dissociate completely when added to water. This makes them relatively easy to model from a chemical standpoint: 1 mole of acid molecules in solution will produce 1 mole of protons.

- Acid solutions can have differing levels of acidity. The strength of an acid solution, or its concentration, is critical to its usefulness. In 1909, no one understood this better than Danish chemist Søren Sørensen, who had taken an interest in the chemistry of proteins—large, complex biomolecules with potent chemical activity. He noted that how acidic a solution was seemed to often have a profound effect on the chemical properties of these complex biomolecules.

- Sørensen decided that he needed a concrete, numerical method for conveying just how acidic or basic a solution was, so that he could maintain proper scientific controls in his experiments. He did this by creating a new scale based on the total concentration of hydrogen ions in solution. But just indicating the concentration of acid or base was cumbersome, and Sørensen wanted something more efficient. The product of his labor was a scale called the pH scale.

THE pH SCALE

		pH		$[H^+]$
LESS ACIDIC	drain cleaner	14	= $-\log 10^{-14}$ M	= 0.00000000000001 M
	bleach	13	= $-\log 10^{-13}$ M	= 0.0000000000001 M
		12	= $-\log 10^{-12}$ M	= 0.000000000001 M
	ammonia	11	= $-\log 10^{-11}$ M	= 0.00000000001 M
		10	= $-\log 10^{-10}$ M	= 0.0000000001 M
		9	= $-\log 10^{-9}$ M	= 0.000000001 M
	baking soda	8	= $-\log 10^{-8}$ M	= 0.00000001 M
		7	= $-\log 10^{-7}$ M	= 0.0000001 M
	pure water	6	= $-\log 10^{-6}$ M	= 0.000001 M
		5	= $-\log 10^{-5}$ M	= 0.00001 M
	tomato juice	4	= $-\log 10^{-4}$ M	= 0.0001 M
		3	= $-\log 10^{-3}$ M	= 0.001 M
	vinegar	2	= $-\log 10^{-2}$ M	= 0.01 M
MORE ACIDIC		1	= $-\log 10^{-1}$ M	= 0.1 M
	battery acid	0	= $-\log 10^{0}$ M	= 1 M

- Sørensen created a useful, compact numerical scale for the reporting of acidity. He used the now-familiar notation “pH” as a shorthand for “power of hydrogen,” because the pH scale is based on the exponent in the hydrogen ion concentration.

- What he may not have realized at the time was that the entire world would soon adopt his system and that more than 100 years later, it would still be the standard method for reporting acidity and basicity of materials. It makes such a useful standard because pH can be quickly converted into a host of useful units to solve a range of problems.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 670–671, 678–684.
Masterton and Hurley, *Chemistry*, 13.1–13.3.

QUESTIONS

1 What are some of the properties of the conjugate bases to our 6 strong acids that help explain why those acids ionize completely in solution?

2 A human stomach in the fasted state (having not recently eaten) is often modelled in the chemistry lab using 0.1 M (molar) hydrochloric acid. What is the approximate pH of stomach contents when fasted?

Answer

2) 0.1 M HCl = 0.1 M H^+; pH = 2.

Weak Acids and Bases

LECTURE 36

Hydrochloric acid and acetic acid solutions of similar concentrations have startlingly different pH values and react with differing intensities in certain systems in which protons participate in reactions. This means that there is something fundamentally different between the 6 strong acids—hydrochloric, hydrobromic, hydroiodic, sulfuric, nitric, and perchloric acids—and all the others. This lecture is focused on bringing all of those other acids into the discussion. To get this discussion started, we have to abandon our way of thinking about how acids ionize.

WEAK ACIDS

› Because we have only investigated strong acids, we could get away with assuming that acids dissociate completely when dissolved in water. Every last molecule of HCl in the mix can be assumed to be H+ and Cl–, meaning that a 1-molar solution of HCl should produce a proton concentration of 1 molar in the resulting solution. But this behavior is the exception, not the rule. All other acids that we will encounter in this course are defined as weak acids, which behave quite differently.

› When we make a solution, for example, of hydrochloric acid, we know that hydrochloric acid is a strong acid and that it's going to dissociate completely (based on the definition of a strong acid) into H+ and Cl–. In a solution of HCl, practically every single molecule of HCl comes apart and forms protons, maximizing the acidity of the solution.

› If we instead make an equal-concentration solution of acetic acid—a weak acid that we know will ionize slightly to form H+ and its conjugate base, acetate, but not completely—only a small fraction of the acetic acid becomes ionized in the solution at any point in time.

- Acetic acid is a disfavored equilibrium. It's weak. Adding a lot of acetic acid will only add a few protons based on the equilibrium behavior. On the other hand, hydrochloric acid is strong because it will ionize 100%, forming as strong of a solution of acid as possible.

- This fundamental difference in the behavior of weak and strong acids means that we can't treat them identically. Because weak acids release only some of their protons into solution, we have to model their behavior differently.

THE ACID DISSOCIATION CONSTANT

- Unlike strong acids, which release their acidic proton into solution never to be reunited, weak acids exercise a greater hold over their acidic hydrogens, giving them up only reluctantly and occasionally.

- We can model the ionization equilibrium for any acidic molecule, using an equilibrium constant called K_a. This will allow us to assign a value to just how weak any given acid is compared to others.

- K_a is no different than any other equilibrium constant, such as K_{eq}. The only reason for the different subscript is because with K_a we're dealing with an acid—the equilibrium between the unionized acid and the ionized acid, which delivers the H+ to the solution. We can determine K_a by using a RICE (reaction, initial, change, equilibrium) table.

- If we know exactly how much of the acid we added to solution, then we know the initial concentration before an equilibrium is established. We can assume that H+ is 0 and A– is 0 for that instant in time when we first add the weak acid to solution.

- A change will quickly happen. Some of that will ionize in a proportional way. This leads to a change in concentration of minus some amount for HA and plus that same amount x for both the proton and conjugate base. This leads us to an expression for equilibrium concentrations that's in terms of only *x*, where we have the initial concentration of the acid minus *x* and 0 plus *x* for the acids (or protons) and for the conjugate base. This gives us an equilibrium problem with just one unknown.

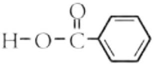
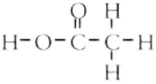
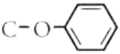
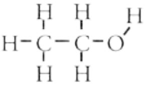
- In this case, K_a for the reaction is equal to H+ times A– divided by HA. We can substitute the variables, or unknowns, into the equation, resulting in an equation in terms of a single unknown, *x*. Now it's *x* times *x* divided by HA minus *x*. We can simplify the equation further by putting the proton concentration in where it belongs and then even condensing the numerator.

R	HA	$\leftrightarrows$	H^+	A^-
I	$[HA]_i$		0	0
C	$-1x$		$+1x$	$+1x$
E	$[HA]_i - x$		x	x

$$K_a = \frac{[H^+]_{eq}[A^-]_{eq}}{[HA]_{eq}} = \frac{x^2}{[HA]_i - x} = \frac{[H^+]_{eq}^{\ 2}}{[HA]_i - [H^+]_{eq}}$$

- Now we have an equation that will yield the K_a value, but the equation is only in terms of 2 things that we can easily measure: the initial concentration of the weak acid and the pH of the solution once equilibrium is established. That means we can determine the K_a for any acid by making a solution of known concentration and then measuring its pH.

- K_a goes beyond just giving us a way to calculate the pH of solutions of weak acids. It also gives us a very useful tool for comparing the relative strengths of weak acids.

ACID	MOLECULAR FORMULA	STRUCTURAL FORMULA	CONJUGATE BASE	K_a	pK_a
Hydrofluoric	HF	$H-F$	F^-	6.8×10^{-4}	3.17
Nitrous	HNO_2	$H-O-N=O$	NO_2^-	4.5×10^{-4}	3.40
Benzoic	$HC_7H_5O_2$		$C_7H_5O_2^-$	6.3×10^{-5}	4.20
Acetic	$HC_2H_3O_2$	 $H-O-\overset{O}{\overset{\Vert}{C}}-\overset{H}{\underset{H}{C}}-H$	$C_2H_3O_2^-$	1.75×10^{-5}	4.76
Hydrochlorous	$HClO$	$H-C-Cl$	ClO^-	3.0×10^{-8}	7.40
Hydrocyanic	HCN	$H-C\equiv Cl$	CN^-	4.9×10^{-10}	9.21
Phenol	HOC_6H_5		$C_6H_5O^-$	1.3×10^{-10}	9.89
Ethanol	C_2H_6O	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H$	$CH_3CH_2O^-$	10^{-16}	16

- Acetic acid has a K_a of 1.75×10^{-5}; it is clearly a weak acid. Phenol, a common ingredient in lip-balm formulations, has a pK_a of 1.3×10^{-10}, making it about 100,000 times less acidic than vinegar. Beverage alcohol, or ethanol, comes in at about 10^{-16}, 1 million times less acidic than phenol.

- But just like proton concentrations in Sørensen's laboratory, acid K_a values cover a huge range of numbers. Our short table of K_a values covers a range of 11 orders of magnitude. So, just like Sørensen's pH scale, we often report the strength of an acid using not its K_a, but its pK_a, or the negative log of the acid dissociation constant.

- When we modify K_a values in this way, we get much more manageable numbers, and just like the pH scale, lower numbers mean a stronger acid. Acetic acid comes in at 4.76 on the pK_a scale. Phenol is at 9.89, and ethanol is at about 16.

- The difference is that pK_a values reference the intrinsic acidity of a particular molecule, giving us information about how easily a particular compound ionizes, while pH refers to the total proton concentration of a solution.

- It is possible to have a very acidic solution of acetic acid, for example, which means a low (very acidic) pH value, but the pK_a of acetic acid lets us know that it will have to be very concentrated if we need such a solution.

DETERMINING THE ACIDITY OF A WEAK ACID SOLUTION

- Once we have determined the dissociation constant for a given acid, it can be used to predict the pH of any solution of that compound that we can imagine. To do this, we simply reverse the equation that we explored previously, making the proton concentration the variable and using the predetermined K_a value to solve.

- We can use the K_a value as a tool to predict exactly what pH will be achieved by a given concentration of weak acid because it accounts for the partial ionization of weak acids.

WEAK ACIDS AND CONJUGATE BASES

- Think about the conjugate base of a strong acid, one like hydrochloric acid. We know that the very definition of a strong acid predicts that its conjugate base—in this case, chloride ion—has no affinity for protons whatsoever. From a Brønsted-Lowry perspective, chloride is neither an acid nor a base; it is completely neutral.

- If chloride had any basic properties at all, at least a small fraction of that chloride would pick up a proton here and there, reversing the process. This would actually be the definition of a weak Brønsted-Lowry base. This means that the weaker an acid becomes, the stronger its conjugate base must be.

- Strong acids have completely neutral conjugate bases, but weak acids do not. As the acid becomes weaker, its conjugate base becomes progressively stronger. So, if acetic acid is a stronger acid than phenol, which is stronger than ethanol, then acetate must be a weaker base than phenolate ion, which is itself a weaker base than ethanolate ion.

THE BASE DISSOCIATION CONSTANT

- So, progressively weaker acids will have progressively stronger conjugate bases. But we can put a number on that strength. How exactly can we convey the intrinsic strength of a Brønsted-Lowry base numerically?

- Water has amphiprotic properties, which means that it can act as both an acid and a base. Water autoionizes in an equilibrium governed by yet another equilibrium constant, K_w. Bases can accept a proton from water to form hydroxide ions in a third equilibrium governed by the constant K_b.

- We can put all 3 of these reactions together to discover that K_a, K_b, and K_w are related to one another. The relationship between K_a, K_b, and K_w leads us to an overall picture of how a solution of weak acid or a weak base will behave. It also gives rise to a number of different relationships between the proton and hydroxide concentrations.

- Consider a standard acid dissociation reaction where HA dissociates to become H+ and A–. Now consider a standard base association reaction using that same conjugate base. If A– is a base, that means it can also react with a molecule of water to create HA and hydroxide ions.

- If we use conjugate acids and bases to make these 2 equations and then add them together, we get the ionization of water, and we know the equilibrium constant for that process: K_w. If we know K_a and we also know that K_w is a constant, we have a mathematical route to get to K_b—specifically, $K_a \times K_b = K_w$.

- Using this expression, we have a mathematical relationship that allows us to calculate the base association constant of any base for whose conjugate acid we know the acid dissociation constant.

- The hydroxide ion concentration times its conjugate acid divided by the base itself is equal to K_b. Mathematically, this is not much different from what we see when we use acid dissociation constants to determine pH. We can use the base association constant to determine pOH if we're creative.

- For a generic reaction, we can create a simplified expression, noting that hydroxide ion concentration is equal to a conjugate acid concentration in the base association reaction. We can make the assumption in most cases that the hydroxide ion concentration at equilibrium for a weak base is much lower than the actual base concentration initially was. Based on some simple substitutions and assumptions, we find that the hydroxide concentration is the square root of K_b times the concentration of the base itself.

- We now have a very quick way to determine the hydroxide ion concentration of any solution made by adding a particular base to that solution. We can, from there, very easily determine proton concentrations, pH's, or anything else we need to answer the problem at hand.

$$\begin{array}{rcll} HA & \longrightarrow & H^+ + A^- & K_a \\ A^- + H_2O & \longrightarrow & HA + OH^- & \underline{K_b} \\ \hline H_2O & \longrightarrow & H^+ + OH^- & K_w \qquad K_aK_b = K_w \end{array}$$

$$K_b = \frac{[OH^-]_{eq}[HA]_{eq}}{[A^-]_{eq}} = \frac{\left([OH^-]_{eq}\right)^2}{[A^-]_i} = [OH^-]_{eq} = \sqrt{K_b[A^-]_i}$$

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 684–690, 693–699.
Masterton and Hurley, *Chemistry*, 13.4–13.5.

QUESTIONS

1 The pH scale can theoretically extend far beyond the 0-to-14 scale that is typically shown in introductory lectures. Why is the scale typically only discussed from 0 to 14 for aqueous solutions?

2 Hypochlorous acid (HClO) is a very weak acid with a pK_a of about 7.5. What is the pH of a 1 M (molar) solution of HClO?

Answer

2) pH = 3.75.

Acid-Base Reactions and Buffers

LECTURE 37

In this lecture, you will consider not just how acids and bases affect the proton and hydroxyl ion concentrations in solutions, but also how acids and bases can react with one another when mixed. You will learn about the proton transfer reaction and how it causes acids and bases to neutralize one another. You will also learn about the effect of mixing weak acids and their conjugate bases. Finally, you will discover how to determine a solution's pH experimentally.

NEUTRALIZATION REACTIONS

› The Brønsted-Lowry definitions of acids and bases tell us that acids are proton donors and bases are proton acceptors. When we put an acid in the presence of a base, a chemical reaction can take place—one in which the acid releases a proton not to water, making a hydronium ion (usually written as a simple proton), but to the base, forming that base's conjugate acid. This very simple chemical reaction is called a proton transfer reaction.

› The simplest scenario involves combining equal amounts of strong acid and base. For this example, let's use hydrochloric acid and sodium hydroxide as reagents. Being a strong acid and a strong base, each will dissociate completely into its constituent ions. But what happens when we combine one equivalent of each compound?

› We have brought 2 reagents together that are creating protons and hydroxide ions in large concentrations. That should immediately set off some alarms for you, because K_w, the equilibrium constant for the ionization of water, is very small, 10^{-14}. High concentrations of protons and hydroxide ions simply cannot coexist. Let's consider what happens when these 2 reactions take place together.

- It's time to consider not just how acids and bases affect the pH of a solution, but how they can react with one another and the effects that has on the pH of a solution. Let's start by addressing the idea of a proton transfer reaction.

- We know that HCl is a strong acid; it is an excellent source of hydrogen ions when it's dissolved in water. We also know that sodium hydroxide (NaOH) is a very strong base, which means that when we dissolve it in water, we get plenty of hydroxide ions.

- When you mix the 2, they have the potential to combine to make water. We know that K_w for water is in favor of that water forming. If we were to mix reagents that are sources of hydrogen ions with other reagents that are sources of hydroxide ions, we expect those 2 to react with one another and form water, a neutral compound.

- If we take this reaction and sum the 2 together, we can remove the hydroxide and protons that have reacted with one another, and the overall reaction, when we add hydrochloric acid to sodium hydroxide, or vice versa, is to make make a salt—in this case, sodium chloride—and water, both of which are neutral.

hydrochloric acid $\quad HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$

sodium hydroxide $\quad NaOH_{(aq)} \longrightarrow OH^-_{(aq)} + Na^+_{(aq)}$

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow \cancel{H^+_{(aq)}} + \cancel{OH^-_{(aq)}} + Na^+_{(aq)} + Cl^-_{(aq)}$$

$$\cancel{H^+_{(aq)}} + \cancel{OH^-_{(aq)}} \longrightarrow H_2O_{(liq)}$$

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow \boxed{\underbrace{H_2O_{(liq)}}_{\text{water}} + \underbrace{Na^+_{(aq)} + Cl^-_{(aq)}}_{\text{salt}}}$$

- Reacting equal amounts of strong acids and bases leads to a completely neutral solution of saltwater. This kind of process is called a neutralization, because the pH effects of both the acid and base are cancelled out in the overall process, leading to a solution of water whose pH is governed simply by water's autoionization constant.

- Neutralization of acids and bases is not only a very common reaction, but one that was understood relatively early in the study of chemistry. Understanding this reaction can prove remarkably useful when trying to adjust the pH of a solution—specifically, not just to a neutral pH of 7, but to any pH that we choose.

STRONG ACID–STRONG BASE REACTIONS

- When a strong acid and a strong base come together in a solution, they're going to react to neutralize one another. What happens if we add a strong base to a strong acid incrementally (for example, sodium hydroxide to a solution of hydrochloric acid)?

- By constantly adding or removing small amounts of strong acid and base, we could, in theory, maintain the pH of a system at a steady level while introducing nothing more than a bit of salt to the solution.

- But that is a lot of work, and it takes a lot of attention to constantly monitor pH and make small adjustments by adding more and more material to the system. It is a really painful exercise to have to go through just to keep the pH of a solution steady. Fortunately, there is a much simpler solution.

WEAK ACID–STRONG BASE REACTIONS

- We have to think about how we are going to determine the concentration of a solution of weak acid as its conjugate base builds up in response to raising pH. Unlike the example of a strong acid–strong base neutralization reaction, which produced only water and salt, this time neutralizing a weak acid produces a weak base, which must be accounted for. Fortunately, we have a useful equation for this purpose.

- For this, we turn to the work of Lawrence Joseph Henderson and Karl Albert Hasselbach, who are most famous for their work surrounding the pH of blood and its effect on oxygen transport. Both men understood that hemoglobin was a vehicle for oxygen, but that the vehicle only worked properly when suitable blood plasma levels were maintained.

- To understand how the pH of a solution will be affected by the presence of a weak acid in its conjugate base in different quantities, we have to use the Henderson-Hasselbach equation. You might see this equation presented in a number of different ways, depending on the application. It can be used to calculate pK_a or pH or the ratio of conjugate acids in bases, depending on how the items in the equation are arranged.

$$pK_a - pH = -\log\left(\frac{[A^-]}{[HA]}\right) \qquad pK_a - pH = \log\left(\frac{[HA]}{[A^-]}\right)$$

$$pH - pK_a = \log\left(\frac{[A^-]}{[HA]}\right) \qquad pH - pK_a = -\log\left(\frac{[HA]}{[A^-]}\right)$$

$$pH = \log\left(\frac{[A^-]}{[HA]}\right) + pK_a \qquad pH = \log\left(\frac{[HA]}{[A^-]}\right) - pK_a$$

- The Henderson-Hasselbach equation is indispensable in the fields of biology, medicine, and chemistry, in which the buffered pH of mixtures can mean the difference between success and failure, or even life and death.

BUFFER SOLUTIONS

- Mixing strong acids and bases can lead to solutions of almost any pH we desire. Simply adding a small bit of strong acid or base to a solution of another alters the pH of that solution quite readily. But what about systems whose pH we don't want to alter? Is there some way that we can stabilize the pH of a solution and make it resistant to change?

- Imagine that you are Søren Sørensen studying the effect of acidity on a variety of biological molecules. But the problem you are encountering is that proteins themselves consume and produce hydrogen ions when dissolved, throwing off the pH of the media that you carefully set at the beginning of the experiment.

- Without a constant pH, experimental control is ruined. Now you have to sit at your reaction flask all day, closely monitoring the pH and adding a drop of acid and a pinch of base just to maintain this simple yet essential scientific control.

- This is exactly that kind of challenge that Sørensen faced. But Sørensen wasn't about to spend all of his time adding acids and bases drop by drop to one another. His solution to this problem was to mix solutions not of strong acids and bases, but of weak acids and bases to achieve media of the appropriate pH for his experiments.

- These mixtures of weak acids and bases have the remarkable ability to resist pH changes all on their own, because protons released into or removed from the solution by other means are balanced as the equilibrium between weak acid and base shifts. Essentially, the weak acids and bases in the system are adding and removing hydrogen ions all on their own.

- By mixing about equal amounts of a weak acid and its conjugate base, Sørensen could make solutions that were stabilized. The greatest resistance to pH change happens when acid and conjugate base concentrations are equal, which means at a pH equal to the $\mathrm{p}K_\mathrm{a}$ of the conjugate acid. So, to select an appropriate buffer for any given pH, all we have to do is find a weak acid with a $\mathrm{p}K_\mathrm{a}$ near the pH of the experiment we want to conduct.

- Buffer solutions are an intrinsic part of chemistry and the world around us. For example, your blood is buffered partially by bicarbonate and carbonic acid. This mixture helps keep your blood between a pH of

7.2 and 7.4. Anything outside of this narrow range is enough to cause medical distress as the hemoglobin in your body fails to transport oxygen correctly.

- Carbonic acid has a pK_a of about 6.4. So, if your blood pH drops precipitously—a condition known as acidosis—the bicarbonate-carbonate buffer system in your blood kicks in, resisting the drop in pH. A number of other buffers, including phosphates, all work in concert to help create a sophisticated system of buffers that protect you from drastic changes in the pH of your blood.

pH INDICATORS

- There is a simple way to determine the pH of a solution experimentally. Sørensen pioneered the use of what are commonly called pH indicators, a class of compounds with 2 very distinct properties: They must absorb colored light very strongly, and they must undergo a proton transfer reaction of their own that alters their color.

- Adolf Von Baeyer was a prolific German chemist who had many interests, including the synthesis of dyes like indigo and a compound he discovered called phenolphthalein. Created from the starting materials phenol and phthalic acid, phenolphthalein didn't catch on as a dye compound, because under neutral pH conditions it is actually colorless.

- But what Baeyer discovered, and what Sørensen summarily exploited, is that phenolphthalein is a weak Brønsted-Lowry acid with a pK_a of about 8.2, and when phenolphthalein loses that acidic proton, it undergoes a chemical change that causes it to absorb green light, creating the attractive shade of fuchsia.

- Many compounds change color in response to changes in pH, but what makes phenolphthalein and other molecules like it very special is that they absorb visible light so strongly that only a minute amount of the compound is needed to give a solution color.

- Just a pinch of this indicator compound in a solution is enough to make the solution change color in response to pH without significantly changing the acid-base chemistry that is going on in the solution.

- Phenolphthalein is not alone in this class of compound. This is a good thing, because the characteristic color change of phenolphthalein only tells us when we pass the pH mark of 8.2. Some other very commonly encountered indicators include thymol blue, which changes from red to yellow at pH 1.2 and then from yellow to blue at pH 8.0. Methyl orange changes from red to yellow at pH 3.1.

- Another indicator is phenol red, which undergoes a gradual shift from yellow to red over a pH range of 6.4 to 8.0. This makes it an ideal choice for testing of pool water for appropriate pH, because the ideal pH of pool water is directly in the middle of this transition.

- By adding just a drop of test solution to a sample of water and comparing the color of the new solution to the color on a reference card, one can quickly and easily verify the pH of a pool or hot tub to be sure that it is just right before jumping in.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 725–739.
Masterton and Hurley, *Chemistry*, 14.1, 14.3.

QUESTIONS

1. One common antacid formulation contains not only the base sodium bicarbonate, but also the acid citric acid. What is the purpose of including this acidic ingredient in an antacid product?

2. Imagine a buffer made by mixing 1 mole of hypochlorous acid (HClO) and hypochlorite ion (ClO^-) in 1 liter of solution. What is the pH of this buffer? If 0.1 moles of sodium hydroxide are added to this buffer, what is the new pH of the solution?

Answer

2) buffer pH = 7.5; after-base-addition pH = 7.59.

Polyprotic Acids

LECTURE 38

In the examples of acids that we have encountered so far, we have been using Brønsted-Lowry acids that have just one acidic proton on them—one acidic hydrogen that can be released into solution. Acids like these are called monoprotic acids, meaning that only one proton can possibly be donated during the dissociation of these molecules. But all acids are not created equal. There are those that have more than one acidic proton; they have an inventory of multiple acidic protons to give up. This lecture is dedicated to these types of acids and their more complex ionization processes.

POLYPROTIC ACIDS

- Polyprotic acids are acids that have more than one acidic proton. A great example is phosphoric acid, which contains 3 hydrogens that could be fairly easily removed to create a conjugate base.

- You might be tempted to conclude that 3 acidic protons in very similar chemical environments would simply all pop off at the same time, creating an equilibrium between phosphoric acid and phosphate ion, a complex anion containing 3 negative charges. But it isn't this simple.

- Deprotonation of weak acids like this one takes place in a stepwise fashion. And phosphoric acid gets stingier and stingier about donating protons as its reserve gets depleted.

- As phosphoric acid begins to release protons, it's not going to let all 3 of them go at once. First, it will release one proton. In doing so, it's going to become dihydrogen phosphate ion and a proton, and there is an equilibrium (K_{a1}) that governs this particular deprotonation process.

MONOPROTIC phosphoric acid

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+$$

POLYPROTIC acetic acid

$$H_3PO_4 \overset{K_{a1}}{\rightleftarrows} H_2PO_4^- + H^+ \overset{K_{a2}}{\rightleftarrows} HPO_4^{2-} + H^+ \overset{K_{a3}}{\rightleftarrows} PO_4^{3-} + H^+$$

$K_{a1} = 6.90 \times 10^{-3}$
$pK_{a1} = 2.16$

$K_{a2} = 6.20 \times 10^{-8}$
$pK_{a2} = 7.12$

$K_{a1} = 4.80 \times 10^{-13}$
$pK_{a3} = 12.32$

- Dihydrogen phosphate still has 2 more potential protons to let go of, and when it lets go of a second proton, there is a second equilibrium (K_{a2}), but this equilibrium is even less favored. This is because we're asking an already negatively charged dihydrogen phosphate to act like an acid and release another proton, gaining yet another unit of negative charge.

- Concentrating that negative on the conjugate base means that the conjugate acid in that step is weaker than the previous one. We have one proton left, so the phosphoric acid can deprotonate yet again. When it does so, it gets 3 negative charges. Now it's a phosphate anion that has 3 minuses and another proton, so this equilibrium is even less favorable. The final deprotonation (K_{a3}) behaves as though it is an even weaker acid than the previous one.

- Polyprotic acids get multiple K_a values. In this case, K_{a1} governs the dissociation reaction in which phosphoric acid is the acid and the dihydrogen is the conjugate base. There is a second equilibrium governed by a K_{a2}, in which dihydrogen phosphate is the acid and hydrogen phosphate anion is the conjugate base. K_{a3} governs the final equilibrium, in which hydrogen phosphate anion is the acid and phosphate anion is the conjugate base.

- Just as the charges on the conjugate bases would lead you to believe, there's a trend in these values: K_{a1} is always larger than K_{a2}, which is always larger than K_{a3}, because we're building up more and more negative charge as we release more and more protons into solution. There's a huge difference in the relative acidities of these K_a values.

- We can't just consider phosphoric acid in equilibrium with phosphate ion if we are going to model this polyprotic acid correctly. We have to include the other species that can form as a result of stepwise ionization. Specifically, dihydrogen phosphate and hydrogen phosphate must also be accounted for.

- Other familiar compounds, such as the strong acid sulfuric acid, can do this. So can some familiar-sounding weak acids, such as the carbonic acid that buffers your blood; the lactic acid that builds up in your muscles, causing soreness as you exercise; and tartaric acid, which is responsible for some of the tart flavors of grapes and wine.

- There are many examples of polyprotic acids, and to be able to understand the sophisticated equilibria that drive the pH of chemical systems, we have to be able to understand and predict their behavior.

PH OF POLYPROTIC ACID SOLUTIONS

- Not all acids are created equal. Not only are there strong acids and weak acids that ionize to different extents, but now we have to consider that polyprotic acids can donate multiple protons to a solution. That leads to an obvious question: Just how important are these second and third deprotonations when it comes to determining the pH of polyprotic acid solutions?

- The good news is that most of the time they can be ignored. If the K_{a2} value is substantially lower than the K_{a1} value, then it can be assumed that the second dissociation happens so rarely that it is not necessary to include it in an estimate of pH.

REACTIONS OF POLYPROTIC ACIDS

- We get lucky with polyprotic acids and their effect on the pH of solutions. Most of the time, we can ignore the minor contribution of second and third deprotonations. But our luck is about to run out as we consider how polyprotic acids behave in other familiar experiments and preparations.

- Consider adding a base to a polyprotic acid like oxalic acid, which has 2 acidic protons. When fully deprotonated, this diprotic acid becomes oxalate, a primary component of many kidney stones. But oxalates aren't all bad.

- The same anion that can make up kidney stones is also a critical component of the anticancer drug oxaliplatin, a compound that wreaks havoc on the DNA of rapidly growing cancer cells, slowing tumor progression in critically ill cancer patients.

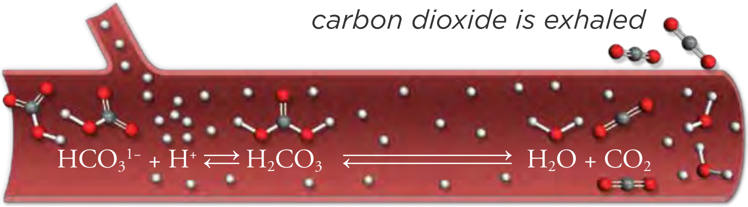
- Whether you are a urologist trying to prevent oxalate from accumulating in your patients' kidneys or an oncologist using it as a life-saving medicine to kill cancer, you can see why the protonation state of this little acid molecule can be critical to the equation.

- In the titration of oxalic acid, the second K_a value isn't negligible like it is for many other polyprotic acids. Instead, it turns out to be critical in determining the conditions under which oxalic acid will become oxalate, with all of the health benefits and perils that come along with it.

BUFFERS OF POLYPROTIC ACIDS

- When it comes to using polyprotic acids in buffers, these multiple-ionization equilibria also have to be carefully considered. The use of polyprotic acids in buffers is not without its complications, but also not without its benefits.

- The buffer in your blood, carbonic acid, is a polyprotic acid used to prevent your blood pH from dropping too far below its optimum of about 7.3. It is the buffering equilibrium between bicarbonate and carbonate that at least in part moderates your blood pH.



$$HCO_3^{1-} + H^+ \rightleftarrows H_2CO_3 \rightleftarrows H_2O + CO_2$$

- Dissolved carbon dioxide creates a certain amount of carbonic acid in equilibrium with hydrogen carbonate. We usually think of carbon dioxide as a bad thing, a waste product of respiration that we exhale to get rid of. But in truth, your body needs a certain amount of carbon dioxide to maintain proper blood chemistry.

- Exhaling too much carbon dioxide, as happens during hyperventilation, causes an imbalance in the dissolved carbonic acid in your blood. Think of it in terms of Le Chatelier's principle. As you hyperventilate and expel more carbon dioxide from your lungs than you should, what will the blood coursing through those lungs do in response?

- The blood will respond to the stress by trying to replace the carbon dioxide to reestablish the natural equilibrium. But that means that the carbon dioxide has to come from somewhere, and it comes from your bloodstream.

- Another way of thinking about this is in terms of Henry's law, which tells us that lowering the partial pressure of carbon dioxide in your lungs should lower its solubility in the blood within them, causing dissolved carbon dioxide to escape.

- As the carbonic acid in your bloodstream decomposes to create that carbon dioxide, the pH regulating effects of the carbonic acid–bicarbonate equilibrium in your bloodstream are lost. With less carbonic acid, blood pH rises. Other buffering systems try to kick in, but if the change is too rapid or drastic, they can be overwhelmed.

- This rise of blood pH is known as respiratory alkalosis. It can cause a host of problems, not the least of which is that hemoglobin, a complex biomolecule that shuttles oxygen to your cells, starts to have trouble releasing its molecular oxygen passengers at their destination. In an odd chemical twist, this means that breathing too rapidly can actually cause your body to starve of oxygen.

- This causes the classic symptoms of dizziness, tingling, and confusion that are associated with hyperventilation. It also explains why the classic remedy of breathing into a paper bag is sometimes recommended.

- This traps the carbon dioxide that you exhale and causes you to re-inhale a greater concentration of carbon dioxide. Both Henry's law and Le Chatelier's principle predict that this remedy should help by encouraging more carbon dioxide to dissolve into the bloodstream and rehydrate to become carbonic acid. It should at least help temporarily while you calm yourself down to the point that your body can get things back to normal.

PHOSPHATE BUFFERS

- Carbonate buffers are hardly the only biologically relevant buffer system. Another polyprotic acid system is phosphate buffers, which are remarkably versatile tools in both your body and in the chemistry lab. Cells use them to maintain the pH of the solutions inside of them, and researchers use them to establish a variety of controlled pH conditions to let them make observations in well-regulated pH conditions.

- What makes phosphates so special? The answer to that question begins with their triprotic nature. Phosphoric acid, dihydrogen phosphate, hydrogen phosphate, and phosphate itself all coexist in equilibrium with one another in aqueous solutions.

- It should come as no surprise that pH buffers meant to emulate physiological bloodstreams nearly always are phosphate buffers, because of the pK_a of dihydrogen phosphate ion. Solutions of these buffers were used by Søren Sørensen to investigate the effects of pH on proteins found in living systems, and they did a remarkable job of this. But these buffer solutions gave him a way to conduct his investigations without any living host to complicate the process.

- What makes phosphates and other polyprotic acid buffers particularly versatile is the fact that buffer solutions can be created at various pH values.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 691–693.
Masterton and Hurley, *Chemistry*, 13.4.

QUESTIONS

1. What are some polyprotic acids that are commonly encountered in food chemistry, and what is their protonation state in the foods in which they are found?

2. Which buffering system would you recommend to maintain a stable pH of 7.2 in a given solution?

   a. Phosphoric acid–dihydrogen phosphate

   b. Dihydrogen phosphate–hydrogen phosphate

   c. Hydrogen phosphate–phosphate

Answer

2) “b” is the best choice, because the pK_a of dihydrogen phosphate is 7.2.

Structural Basis for Acidity

LECTURE 39

Some acids ionize with great efficiency in solution, while others ionize only slightly in an equilibrium process governed by the constant K_a. The smaller K_a, the less dissociation takes place, and therefore the weaker the pH of the resulting solution. But why is there a difference in the ease with which various acids ionize? To answer this question, this lecture will invoke electronegativity, molecular geometry, hybridization, covalent bonding, and a host of other concepts from previous lectures. But it all boils down to 2 simple questions: How much charge is on the atom bonded to the acidic hydrogen, and how stable is the conjugate base?

BOND POLARITY

- The first stop in our discussion of how easily acids dissociate is to consider just how stable an acid molecule is. Humphry Davy got us started on this by correctly identifying hydrogen as the critical element for acidity.

- A compound must have a hydrogen that it is willing to let go of as a hydrogen ion if it is to meet the Brønsted-Lowry definition of an acid. What does it mean to release a hydrogen ion from a molecule? It means that the electrons from the bond to the hydrogen need to be taken on completely by the other bonded atom. This results in a full positive charge on the hydrogen, a full negative charge increase on the conjugate base, and the separation of the 2 into solution.

- So, if breaking the bond means completely separating the charge, we can think of polar bonds as being already on their way to breaking in this process. In other words, more polar bonds to the hydrogen should mean stronger acids.

- In some sense, this notion works. Consider hydrochloric acid, one of the 6 strong acids: hydrochloric, hydrobromic, hydroiodic, sulfuric, nitric, and perchloric acids. Chlorine, with its high electronegativity, pulls the bonding electrons closer to it even when bonded to hydrogen. Chlorine wants those electrons, and it wants them badly. So, as soon as hydrochloric acid hits water, it dissociates and the proton is released.

- As a general rule, we can use the polarity of the bond to the acidic hydrogen to gauge the strength of an acid. As we work our way from the left to the right across any given row of the periodic table, there is a trend of increasing acidity in binary acids as bond polarity increases. As we work our way across rows of the periodic table, binary acids become increasingly stronger, because each step to the right takes us to a more electronegative bonding partner for the acidic hydrogen.

- This helps explain why hydrocarbons have essentially no acidic character, why deprotonation of ammonia is rarely even considered a real possibility in chemistry, why water's ionization (though significant) is very small, and yet hydrofluoric acid is strong enough that it is used to etch glass.

THE ROLE OF CONJUGATE BASES IN ACIDITY

- It might seem strange that in our quest to understand acid strength we often have to analyze the structure of its conjugate base. This, however, is an overriding tenet in thermodynamics. For any equilibrium process—proton transfer included—the free energy (or stability) of the products is every bit as important as the free energy (or stability) of the reactants.

- So, we have to be wary of the possibility that there will be additional considerations involving the conjugate bases of certain acids, which may counteract the instability introduced by more polar bonds to the acidic hydrogen.

CONJUGATE BASE SIZE

- Another form of binary acids is the hydrohalogens: hydrofluoric acid, hydrochloric acid, hydrobromic acid, and hydroiodic acid. If we consider this series of binary acids using elements not in a given row, but instead in a group, something changes.

- Even though the dipole of hydrofluoric acid (HF) is greatest, it is the weakest acid. Even though the dipole of hydroiodic acid (HI) is the weakest of all, it is the strongest acid, beating out hydrobromic acid (HBr) by a slight but meaningful margin. This flies directly in the face of our method of using bond dipoles to assess acidity. Shouldn't the trend be reversed?

- There must be a more influential force behind the trend in acidity for binary acids as we move down a column of the table like the halogens. As we progress down a row of the periodic table, electronegativity decreases, but the size of atoms and ions increases dramatically because we are adding new valence shells to their electron clouds.

- This increase in volume means that chlorine can disperse negative charge over a greater volume than fluorine can. Neither of these can stack up to bromine's ability to distribute charge, and iodine, with its valence shell in the fifth energy level, is the undisputed king of charge distribution within the group.

- Even the mighty HF dipole is not enough to compensate for the fact that larger halide ions, such as chloride, bromide, and iodide, distribute charge more effectively over a greater volume. To exist, fluoride ion has to pack that negative charge into a small second-energy-level valence shell, and that charge density is its undoing.

- In general, when comparing binary acids of similar structure, we can make the assertion that conjugate bases with better charge distribution are responsible for stronger acids. This trend holds in many cases for other weak acids whose conjugate bases bear localized negative charges.

- For example, compare water (H_2O) to dihydrogen sulfide (H_2S), hydrogen selenide (H_2Se), and hydrogen telluride (H_2Te)—the acids used to debunk Lavoisier's theory that oxygen is the essence of acidity. We see a very similar trend to halogens: decreasing pK_a values as we move down the periodic table. This is because the resulting conjugate bases require that a negative charge resides on the group-6 element. Oxygen, being the smallest of these elements, can only distribute this charge over a very small volume.

- Sulfur, selenium, and tellurium, however, have increasingly larger electron clouds around which they can distribute charge, increasing the overall stability of the hydrogen sulfide, hydrogen selenide, and hydrogen telluride ions.

- When it comes to conjugate base stability, size matters. All other factors considered equal, larger, more polarizable conjugate bases have stronger conjugate acids.

OXYACIDS

- Most simple binary acids, such as the hydrogen halides that we have investigated so far, do not contain oxygen. Some of them were actually first cited as arguments against Lavoisier's postulate that oxygen was the essence of acidity.

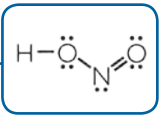
- What drove Lavoisier to advocate his now-disproven theory that oxygen is the essence of acidity? When he made it, his attention was focused on yet another trend in acidities of a series of compounds known as oxyacids.

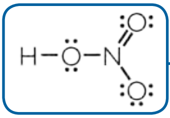
- Oxyacids are a bit more complex than binary acids. They are a class of chemical compounds that contain an O-H bond chemically bonded to a central atom. Don't confuse this with the OH– hydroxide ion from Arrhenius's base definition; here, we are talking about an OH motif that is covalently bonded to at least one other atom.

- Nitric, sulfuric, and phosphoric acids all fall into this class of compound. Other oxyacids, including nitrous, sulfurous, and phosphorous acids, are based on combinations of the same types of atoms. Every one of these oxyacids has at least one acidic proton bonded to an oxygen. This means that the oxygen will be taking on a negative charge when the acid dissociates. So, the effect of conjugate base size and polarizability has been essentially removed in this group.

- Let's examine the $\mathrm{p}K_\mathrm{a}$ values for these acids. Consider the first acid dissociation for each. There is a trend: Nitric acid is stronger than nitrous, sulfuric acid is stronger than sulfurous, and phosphoric acid is stronger than phosphorous. In all 3 cases, decreasing the number of oxygen atoms bound to the central atom correlates with decreasing the acidity of the compound.

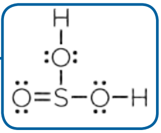
NITROUS ACID

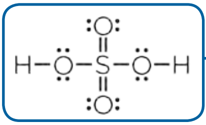




NITRIC ACID

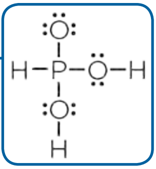
SULFUROUS ACID

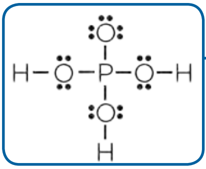




SULFURIC ACID

PHOSPHOROUS ACID





PHOSPHORIC ACID

- This is no coincidence. Other oxyacids follow the same trend. A classic example of this is the oxyacids of chlorine: perchloric, chloric, chlorous, and hypochlorous acids. Hydrochloric acid clearly doesn't belong in this group, because the acidic hydrogen in HCl is attached to the chlorine. Here, instead, the acidic hydrogen is bonded to an oxygen atom. Within this group of oxyacids, as the amount of oxygen decreases, their pK_a's increase, reflecting a decrease in acidity.

- It is easy to see how Lavoisier might have reached his erroneous conclusion about oxygen and its relationship to acidity. In all of the examples we have looked at so far, the addition of more oxygen atoms increases the intrinsic acidity of each class of oxyacid.

- But if oxygen isn't the fundamental source of acidity, why does it seem to bolster the strength of these acids when its ratio in them is increased? The answer lies in oxygen's potent electronegativity: 3.5 on the Pauling scale, just about the highest of all elements.

- Consider the chlorine-containing oxyacids. Hypochlorous acid has only one oxygen bonded to the chlorine atom. The oxygen is going to pull on the electron cloud of that chlorine atom, creating a mild charge separation that makes chlorine more positive and the oxygen more negative.

- The oxygen is reluctant to release a proton, which would cause an even greater buildup of negative charge right where negative charge from the bond dipole already exists. This means that hypochlorous acid is a weak acid with a pK_a of about 7.5, which is more than 10,000 times weaker than acetic acid, or vinegar.

- When we add another oxygen to make chlorous acid, something changes. That second oxygen is pulling the other direction, against its sibling on the other side of the chlorine. This gives the chlorine an even greater positive charge.

- The increased positive charge on the chlorine makes it pull against the oxygen containing the acidic proton even more, and it begins to win the tug-of-war. Now the oxygen bearing the acidic proton is losing some of that negative charge density that made it so reluctant to release its proton in the first place, and the pK_a of chlorous reflects this at about 1.9, more than 100,000 times as acidic as hypochlorous acid.

- Add another oxygen to make chloric acid, and yet another to make perchloric acid, and the effect is amplified each time, creating acids with pK_a values of −1 and about −10, respectively. In fact, both of these would be considered strong acids by rule because their pK_a values are negative, meaning that practically every molecule in a sample of these acids would be ionized in solution.

- Another way to think of this is again to consider the stability of the conjugate bases that form. With each progressive addition of oxygen, the conjugate bases of these oxyacids have less and less localized negative charge. It is instead distributed over progressively more and more chlorine-oxygen bond dipoles. And distributing charge leads to greater stability.

- Unfortunately for Lavoisier, he had no way of knowing in his time that the true nature of oxygen was not to act as an acid itself, but to function as an electron withdrawer in oxyacids, weakening the acidic oxygen's hold on the true source of acidity—its hydrogen.

RESONANCE

- Werner Heisenberg's revelations about electron mobility in molecules led Linus Pauling, Gilbert Lewis, and others to rethink the nature of chemical bonding. Electrons like their freedom. They want to move through larger volumes of space, and that means that more resonance means more stability, not only in neutral molecules, but also in ions.

- All other things being equal, conjugate bases with greater resonance delocalization of their negative charge must be more stable. True to the assertion that conjugate base stability matters, the inclusion of just a bit of resonance stabilization in a conjugate base can have a profound influence on the acidity of a compound.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 702–706.

QUESTIONS

1 Some polyprotic acids have drastically different pK_{a1} and pK_{a2} values. For example, phosphoric acid's 3 acidic protons have pK_a values of about 2.2, 7.2, and 12.3. On the other hand, citric acid's protons have pK_a values of about 3.1, 4.8, and 6.4—much more similar to each other than those for phosphoric acid. How can the molecular structures of these 2 acids explain this difference?

2 The H-F bond dipole is the strongest of any acidic hydrogen. Why, then, is hydrofluoric acid actually a weak acid and not a strong one?

Electron Exchange: Redox Reactions

LECTURE 40

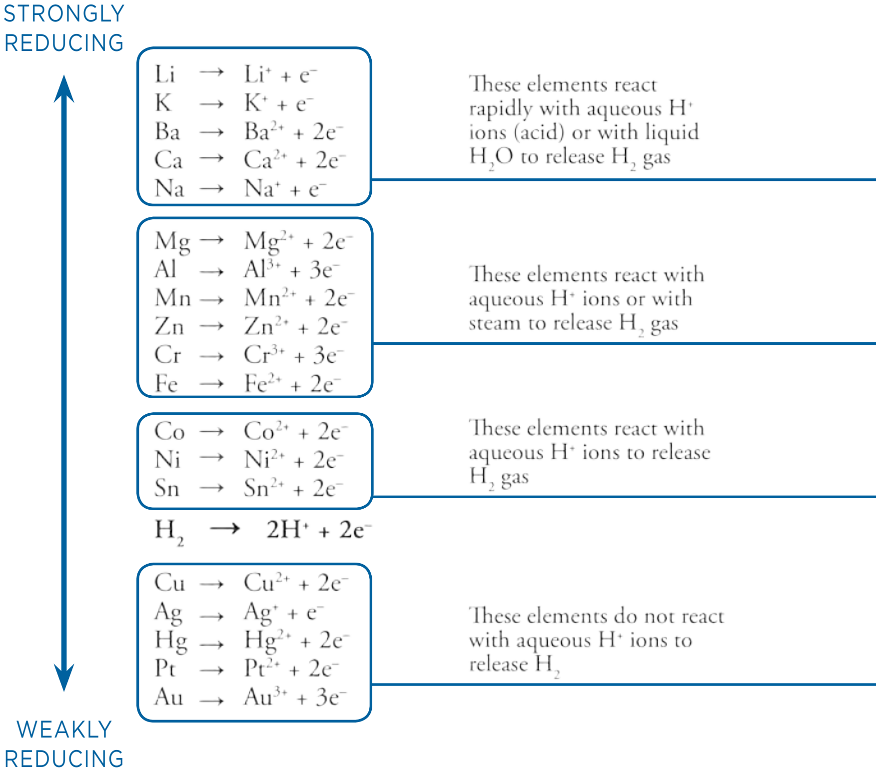
Small, fast-moving, and negatively charged, electrons are usually held tightly by the nucleus to which they belong, giving an element many of its properties. But electrons aren't confined to a single atom or even ion; electrons are often exchanged between and among elements in chemical processes. In ionic bonding, electrons are exchanged between 2 neutral atoms to form ions, and the activity series predicts how some metals might react with one another or with hydrogen ions. But that only scratches the surface of the complex chemistry that can happen when electrons are on the move. In this lecture, you will learn about reduction-oxidation, or redox, reactions.

THE ACTIVITY SERIES

- Think about the metals that are used to make coinage: gold, silver, copper, and platinum. Aside from their relative rarity and beautiful luster, there is another reason that historically these metals in particular are used to make most of the coins used by society as currency.

- For a coin to have value, it has to last. There were other metals available to early cultures—metals like iron—but those metals are prone to react with oxygen in the air, or even the acids in moisture carried by human hands. Over time, they would become dull, their impressions worn and sometimes lost. This process is the result of the iron atoms losing electrons—ultimately to oxygen—to form a new compound in which the iron is now an ion.

- Certain metals are quicker to give up their electrons to form ions than others. When we organize them in a column from most reactive to least reactive, we get what is called the activity series, which gives us a useful guide to compare how easily a metal will become a cation. We can use this table to determine whether or not a certain metal substitution reaction will take place—a reaction in which one metal ion meets another metal in its neutral state and the 2 switch roles by electron transfer.



$Li \rightarrow Li^+ + e^-$
$K \rightarrow K^+ + e^-$
$Ba \rightarrow Ba^{2+} + 2e^-$
$Ca \rightarrow Ca^{2+} + 2e^-$
$Na \rightarrow Na^+ + e^-$

These elements react rapidly with aqueous H^+ ions (acid) or with liquid H_2O to release H_2 gas

$Mg \rightarrow Mg^{2+} + 2e^-$
$Al \rightarrow Al^{3+} + 3e^-$
$Mn \rightarrow Mn^{2+} + 2e^-$
$Zn \rightarrow Zn^{2+} + 2e^-$
$Cr \rightarrow Cr^{3+} + 3e^-$
$Fe \rightarrow Fe^{2+} + 2e^-$

These elements react with aqueous H^+ ions or with steam to release H_2 gas

$Co \rightarrow Co^{2+} + 2e^-$
$Ni \rightarrow Ni^{2+} + 2e^-$
$Sn \rightarrow Sn^{2+} + 2e^-$

These elements react with aqueous H^+ ions to release H_2 gas

$H_2 \rightarrow 2H^+ + 2e^-$

$Cu \rightarrow Cu^{2+} + 2e^-$
$Ag \rightarrow Ag^+ + e^-$
$Hg \rightarrow Hg^{2+} + 2e^-$
$Pt \rightarrow Pt^{2+} + 2e^-$
$Au \rightarrow Au^{3+} + 3e^-$

These elements do not react with aqueous H^+ ions to release H_2

EASE OF OXIDATION INCREASES

METAL	OXIDATION REACTION				
lithium	$Li_{(s)}$	→	$Li^{+}_{(aq)}$	+	e^-
potassium	$K_{(s)}$	→	$K^{+}_{(aq)}$	+	e^-
barium	$Ba_{(s)}$	→	$Ba^{2+}_{(aq)}$	+	$2e^-$
calcium	$Ca_{(s)}$	→	$Ca^{2+}_{(aq)}$	+	$2e^-$
sodium	$Na_{(s)}$	→	$Na^{+}_{(aq)}$	+	e^-
magnesium	$Mg_{(s)}$	→	$Mg^{2+}_{(aq)}$	+	$2e^-$
aluminum	$Al_{(s)}$	→	$Al^{3+}_{(aq)}$	+	$3e^-$
manganese	$Mn_{(s)}$	→	$Mn^{2+}_{(aq)}$	+	$2e^-$
zinc	$Zn_{(s)}$	→	$Zn^{2+}_{(aq)}$	+	$2e^-$
chromium	$Cr_{(s)}$	→	$Cr^{3+}_{(aq)}$	+	$3e^-$
iron	$Fe_{(s)}$	→	$Fe^{2+}_{(aq)}$	+	$2e^-$
cobalt	$Co_{(s)}$	→	$Co^{2+}_{(aq)}$	+	$2e^-$
nickel	$Ni_{(s)}$	→	$Ni^{2+}_{(aq)}$	+	$2e^-$
tin	$Sn_{(s)}$	→	$Sn^{2+}_{(aq)}$	+	$2e^-$
lead	$Pb_{(s)}$	→	$Pb^{2+}_{(aq)}$	+	$2e^-$
hydrogen	$H_{2\,(s)}$	→	$2\,H^{+}_{(aq)}$	+	$2e^-$
copper	$Cu_{(s)}$	→	$Cu^{2+}_{(aq)}$	+	$2e^-$
silver	$Ag_{(s)}$	→	$Ag^{+}_{(aq)}$	+	e^-
mercury	$Hg_{(l)}$	→	$Hg^{2+}_{(aq)}$	+	$2e^-$
platinum	$Pt_{(s)}$	→	$Pt^{2+}_{(aq)}$	+	$2e^-$
gold	$Au_{(s)}$	→	$Au^{3+}_{(aq)}$	+	$3e^-$

- We simply treat the reaction like a tug-of-war for the available electrons. Who wants them more?

- For example, a sample of solid zinc in the presence of a copper sulfate solution will dissolve and form zinc ions even as the copper precipitates from the solution. This is because copper is lower on the activity series. It wins the contest for electrons with the zinc and becomes neutral, losing its stabilizing ion-dipole interactions with water. This makes it come out of solution.

- But if that zinc is instead dropped into a solution of magnesium nitrate, nothing happens. Magnesium metal is higher on the activity series, so it is more inclined to stay ionized and let zinc keep its electrons.

- The activity series also naturally clusters metals into groups based on their reactivity with other common materials: those that do not react to produce hydrogen gas, those that react with acids to form hydrogen, those that react with acids and steam to form hydrogen, and those that will even react with liquid water to produce hydrogen gas.

REDUCTION AND OXIDATION

- Chemists break these types of changes down into 2 fundamental types of electrochemical processes: reduction, in which electrons are added to a substance, and oxidation, in which electrons are removed from a substance.

- For example, an atom of iron (Fe) has 26 electrons in its neutral form, but in one of its more common dissolved forms, it is missing 2 of those electrons to form Fe^{2+}. So, iron just lost 2 electrons to become a divalent cation, meaning a +2 charge. This process of losing electrons is called oxidation. In other words, we would say that iron was oxidized to Fe^{2+}.

- Oxygen does not have to be participating in a process for electrochemical oxidation to take place. The name "oxidation" stems from the strong power of oxygen to carry out this process on other materials, but there are many others that can get the same job done.

- In the overall reaction of the dissolution of iron in aqueous acid, 1 mole of iron becomes 1 mole of Fe^{2+} ions as 2 moles of hydrogen become 1 mole of hydrogen gas. The reduction half-reaction is that of protons to hydrogen gas, and the oxidation reaction is that of Fe to Fe^{2+}.

- In this example, it is clear that electrons have been fully transferred from the reducing agent, iron, to the oxidizing agent, protons. But it isn't always that obvious. Redox reactions can also take place between and among covalent substances.

- A simple example of this is the combustion of hydrogen to form water. In this reaction, diatomic hydrogen and diatomic oxygen, each with an oxidation state of 0, react to form water. Water is not an ionic compound, but if we are going to treat this reaction as a redox process, we have to consider what the charges on those atoms would be if water were ionic.

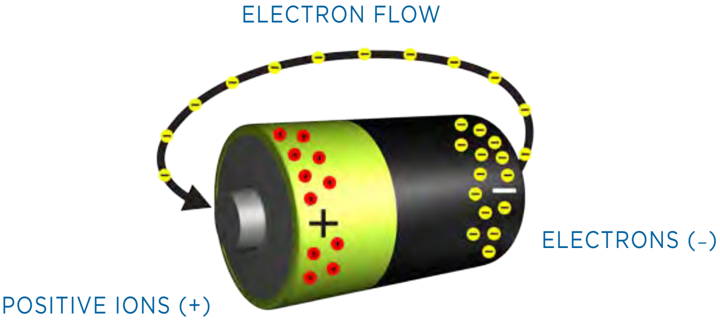
- In this case, the answer is +1 for hydrogen and −2 for oxygen, because oxygen's higher electronegativity gives it greater claim to the electrons participating in bonding, even if not giving it total claim to them.

- Using this simple method of assigning oxidation numbers, we can think of many different types of reactions in terms of reduction and oxidation.

REDOX POTENTIALS

- Our understanding of reduction and oxidation half-reactions gives us more than just a way of describing where electrons are going. Once we have defined these half-reactions, we can use them to predict the chemical potential energy behind any given redox process.

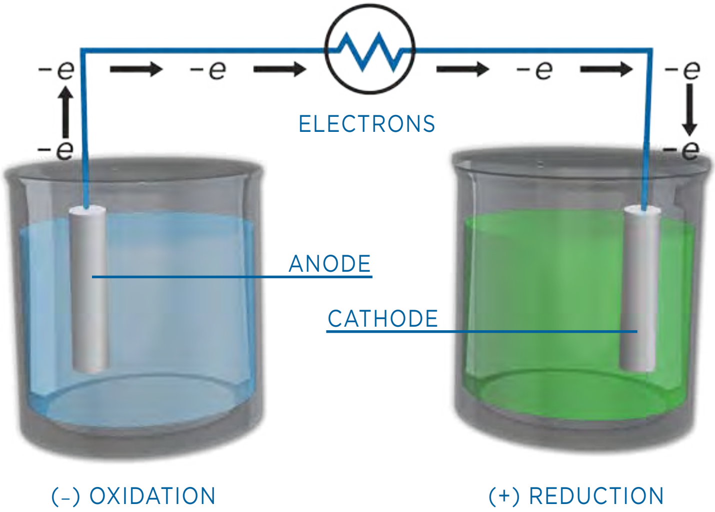
- We can think of redox reactions almost like discharging a battery. The difference is one of scale. A single atom or ion exchanging electrons with another in direct contact might not seem too exciting, but it is exactly the same process that is going on when you turn on your laptop or push the start button on your vehicle, with a few engineering tricks to harness the voltage.



- Just like a battery, a simple redox reaction taking place inside of a flask between individual atoms and ions will have an associated voltage. Voltage is sometimes called electromotive force (EMF), which better describes what the term means. It is a measure of the difference between 2 agents' desire to possess the electrons being transferred. If a reaction's EMF voltage is positive, then the reaction will proceed spontaneously.

- This EMF is much easier to observe when the reduction and oxidation processes are separated from one another. If the reducing agent and oxidizing agent are separated by a conductive substance like a wire, the electrons will have to flow through that wire from the reducing agent to reach the oxidizing agent.

- The side from which electrons flow is called the anode, and the side to which they flow is called the cathode. They don't necessarily have to be charged, but the names help us remember which side is losing electrons and which is gaining them.



- If one side of the system wants the electrons much more than the other, then a strong current will be observed, because the EMF is greater. When both sides have similar desire for the electrons, little or no current is observed, because the EMF is much smaller.

- The EMF for a given redox reaction is all about relative desire for electrons. But atoms and ions don't "desire" anything; they simply attract electrons with differing affinity. As scientists we want to quantify this, but how?

- The key is to realize that there are always 2 opposing forces acting on electrons in a redox process: one pulling them one way and one pulling them another. These opposing forces are called half-cell potentials, and it is the sum of these potentials that tells us just how powerful the EMF will be for a given redox reaction under standard conditions.

- We can use the electromotive force to determine whether or not a reaction will take place. The potential for the entire reaction is simply the sum of the electromotive forces for both half-reactions. In other words, *E* for the overall reaction is equal to the reduction potential for the reduction plus the oxidization potential for the oxidization half-reaction: $E^0_{rxn} = E^0_{red} + E^0_{ox}$.

- That's a pretty simple mathematical relationship, but we have to be careful about our signs. If the reduction potential is negative, instead of adding the oxidization potential, subtract the reduction potential. Mathematically, that should give us the same answer. The other way to do this is to recognize that the reduction potential is supposed to be positive if we're dealing with an oxidation half-reaction.

- There are 2 very important differences that we need to remember for the remainder of our discussion of electrochemistry. First, half-reaction potentials are intensive properties. This means that they do not depend on amounts and therefore are not affected by reaction coefficients the way that enthalpy, entropy, and free energy are.

- Second, greater positive potentials indicate progressively more and more spontaneous reactions. This is the exact opposite of Gibbs free energy values, which become more and more negative as reactions become more favored.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 848–859.
Masterton and Hurley, *Chemistry*, 4.4.

QUESTIONS

1 How can the activity series explain why pure iron and pure aluminum are not recommended for buried water pipe applications where slightly acidic rainwater may reach the pipe? What potentially damaging reaction can occur?

2 Identify the reducing agent and oxidizing agent in the following reaction:

$$Au^{+}{}_{(aq)} + Ag_{(s)} \rightarrow Au_{(s)} + Ag^{+}$$

Answer

2) $Au^{+}{}_{(aq)}$ is the oxidizing agent. $Ag_{(s)}$ is the reducing agent.

Electromotive Force and Free Energy

LECTURE 41

We can combine the half-reaction potentials to determine the electromotive force (EMF) potential for a given redox reaction. That is a useful value, but the benchmark for reaction spontaneity isn't voltage—it's free energy. This lecture is dedicated to bringing redox reactions into the fold and connecting EMF with free energy. As you will learn in this lecture, the real usefulness of redox reactions in chemistry and engineering is not simply in knowing if they will progress, but how much chemical energy is released when they do. This quest will introduce us to 3 of the greatest chemical minds in human history.

MILLIKAN'S EXPERIMENT

- A young theoretical physicist named Robert Millikan, who was working at the University of Chicago in the first decade of the 1900s, made it his personal quest to determine the charge on a single electron, knowing that this value would be critical to someday unlocking the secrets of electrochemical reactions.

- But how can this be done? A single electron is much too small to isolate using the technology available to Millikan more than a century ago, yet he did succeed in obtaining this measurement with remarkable accuracy.

- Millikan was able to get his value using a device that suspends charged oil droplets in magnetic fields. In his ingenious experiment, Millikan generated droplets of oil by spraying them through a very small nozzle into a vacuum. Once these droplets were free of the nozzle, gravity was free to act on them, pulling them downward into a second chamber.

- In this second chamber, Millikan used an X-ray source to ionize the droplets, giving them negative charge. So, these oil droplets now had varying degrees of negative charge. Some may have picked up only a few electrons, while others may have picked up many.

- Millikan had no idea how many each picked up. This may seem like an obstacle. But remember that electrons are incredibly small compared to the mass of atomic nuclei, so adding electrons to these oil droplets should not appreciably change the mass of each droplet.

- At this point in the experiment, droplets would simply continue to fall through the second chamber, except for one factor. The second chamber contained 2 electrodes: one above and one below. With the electrodes off, there was no electromagnetic field in the chamber, so droplets indeed simply fell through at a velocity consistent with their mass.

- But when the electrodes were turned on and began to generate a positive charge in the top and a negative charge on the bottom of the vessel, the speed of the falling droplets began to slow as the negative charge at the base repelled the oil droplets and the positively charged plate at the top of the chamber attracted them.

- By setting the charge separation carefully and measuring the exact field strength needed to levitate a given oil droplet, Millikan could calculate the charge on that droplet.

- How did this help him measure the charge on a single electron? After all, the droplets had many electrons giving them charge. The secret lies in the same logic used by Dalton to prove his atomic theory a century earlier: multiple proportions.

- Millikan repeated his experiment many times, and all of the total droplet charges that Millikan measured were whole-number multiples of a very small number: 1.6×10^{-19} coulombs, which is the charge on a single indivisible electron.

- It was an ingenious way to elucidate the charge of a single particle that was much too small to isolate using the technology available at the time—so ingenious that this tiny number won Millikan a very big Nobel Prize in Physics in 1923, about 50 years before technology would allow us to actually isolate a single electron for study.

FARADAY'S CONSTANT

- Millikan had successfully determined the charge on an individual electron. This was an extremely valuable measurement in and of itself, but in the world of chemistry and physics, a different value has become the most commonly used value for reporting the charge on electrons: the charge not on a single electron, but on a mole of electrons.

- When we look at reactions, and particularly the coefficients on reactions, we usually mean moles, not individual atoms or molecules. So, by multiplying Millikan's charge by a mole, we get 96,485 coulombs per mole of electrons.

- This value is remarkably useful in the quest to tie electromotive force (EMF) to free energy. This value is named Faraday's constant in honor of Michael Faraday, one of the original electrochemists who started us on our way to understanding how the flow of electrons is tied to chemical free energy.

- Faraday is widely regarded as the father of modern electromagnetism. As a young man in England, Faraday had the fortune of being offered an apprenticeship with a local bookmaker. His 7-year apprenticeship exposed him to many books, and it is widely believed that his reading during his teenage years is what inspired him to attend lectures by the revered Humphry Davy.

- Faraday took detailed notes of Davy's lectures—about 300 pages worth—which he then sent to Davy in a letter. Faraday's obviously deep and abiding interest in chemistry caught Davy's attention, leading Davy to offer him an assistantship in his laboratory. Faraday's life was forever changed. This is because Davy was one of the first electrochemists. He was one of the first to use electrical current to induce chemical reactions.

- For part of his career, Faraday continued some of Davy's work, and he drew a correlation between the amount of a reagent that could be oxidized or reduced when a specific amount of current was applied to it. He found that increasing the current (or amount of electrons) flowing into or out of a substance increased the amount of that substance that was reduced or oxidized, respectively.

- Although Faraday's career predates Millikan's, the contribution of Faraday to electrochemistry prompted Millikan and others to name the molar charge of electrons the Faraday constant in his honor.

- Faraday's constant allows us to relate the free energy change to the electromotive force for any given reaction, and it helps us use an equation that reconciles both the issues of sign and the issue of the stoichiometry, or the coefficients in a reaction.

- The equation is the free energy change (ΔG^0) for any redox reaction is equal to minus the total number of electrons exchanged in the process times the Faraday constant—the charge on a mole of electrons, or 96,485 to be exact—times the EMF at standard conditions (E^0): $\Delta G^0 = -nFE^0$.

- The Faraday constant gives us a way to get back and forth between the electrochemical world and the free-energy world. Free energy equals moles of electrons times Faraday's constant times the cell potential, in this case under standard conditions. This results in a unit of coulomb-volts. A coulomb-volt is equal to a joule.

- This equation gives us a way to determine the overall free energy change in the redox process. All we need to know is the cell potential and the number of electrons that are exchanged during that redox process.

THE NERNST EQUATION

- Walther Nernst was a well-established researcher in the German system in the early 1900s. But he was also an inventor. Nernst had already created a special lamp that used ceramic filaments to generate light—a significant improvement over the carbon-based lamp used by famed American inventor Thomas Edison.

- Having bested Edison's design, Nernst became a wealthy and revered scientist. With wealth and recognition come opportunities—opportunities to pursue whatever problems you want to solve, and Nernst had one in mind.

- Nernst was a consummate electrochemist. Devices like his lamp relied on the flow of electricity to operate. Electricity is simply electrons flowing through wires or other conductive media. Just like in chemical reactions, the electrons have to come from somewhere and have a destination.

- But so far, the Faraday constant has only allowed the free energy to be calculated for processes under standard conditions—0° centigrade and concentrations of 1-molar reagents for all species involved. This is more than a bit limiting, and Nernst was a man of practicality.

- What if we could vary the concentrations of reactants and products in electrochemical reactions? If so, then the EMF should change. Faraday's equation did not account for this. Nernst wanted an equation for all occasions, but there wasn't one. So, he came up with one.

$$E = E^0 - \frac{RT}{nF} \ln Q$$

$$E = E^0 - 2.303 \frac{RT}{nF} \log Q$$

- The Nernst equation relates the standard EMF for a reaction to the EMF at any conditions that we can imagine, including changes in temperature and changes in concentration of the reactants. There is a natural log in one of the versions of this equation, but you might also see the Nernst equation written in a base-10 log format.

- To convert the first version of the equation into the second version of the equation, we simply have to add a factor of 2.303 to the pre-log term. This is one of the more preferred forms of the equation. Either one of these are mathematically equal and will give you the same result as long as you're careful to either use the pre-logarithmic factor or the natural log.

READING

Barkan, *Walther Nernst and the Transition to Modern Physical Science*.
Brown, LeMay, and Bursten, *Chemistry*, pp. 860–877.
Masterton and Hurley, *Chemistry*, 18.1–18.4.

QUESTIONS

1. How does the Nernst equation help explain why car batteries struggle more in colder temperatures?

2. Consider the following reaction between silver ions and copper metal:

   $Hg^{2+}{}_{(aq)} + Cu_{(s)} \rightarrow Hg_{(l)} + Cu^{2+}{}_{(aq)}$

   $E^0 = 1.20$ volts

   Based on the given standard EMF (E^0), what is the EMF of this reaction at standard temperature when mercury ion concentration is 0.01 M (molar) and copper ion concentration is 1 M?

Answer
2) 1.14 volts.

Storing Electrical Potential: Batteries

LECTURE 42

Although there is evidence that ancient peoples as long ago as 2500 B.C. might have had a modest command of electricity, the origin of the term "battery" can be found in much more recent history. Notable American statesman and researcher Benjamin Franklin is generally credited with first using the modern name for electrical storage devices, but our modern understanding of them finds its origins in late-18th-century Italy, where 2 fathers of modern electrochemistry, Alessandro Volta and Luigi Galvani, were engaged in an argument. In this lecture, you will learn how this argument led to the development of modern batteries.

ELECTRICAL STORAGE BATTERIES

- Galvani had placed the legs of recently dissected frogs on brass hooks for observation. He noticed that when he touched the brass hook with a probe made of a different metal, the legs twitched. He knew that electrical impulses were associated with muscle contraction, and his conclusion was that he had tapped a new form of electricity—one generated by the muscles in the frog legs.

- But Galvani's contemporary, Volta, believed that the twitching of the muscles was not the source of electric current, but rather a consequence of it. Volta's theory was that the frog legs did not generate current, but rather that they were responding to a current created when 2 different metals—in this case, the brass hook and iron probe—were brought into contact.

- Galvani's theory centered on biologically produced current, and Volta's contrary theory stated that current could be generated without biological material. To prove Galvani wrong, Volta constructed an apparatus that could create current without the aid of a biological component.

- Volta piled alternating discs of silver and zinc, each separated by a disc of leather, cardboard, or some other insulating material. The separating material was soaked in a solution of salt before being placed on the pile. When the top of the pile was connected to the bottom with a conductive wire, an electrical current could be observed flowing from one end to the other.

- Volta's construct looks quite crude in comparison to modern batteries, but it was the first real example of sustained, steady electrical current produced under controlled conditions. It was very quickly realized by many preeminent scientists of the day just how useful Volta's creation could be in research as fundamental as discovering elements.

MODERN BATTERIES

- Today's batteries look a bit different than voltaic piles did about 200 years ago. They all operate on the same principle: Reduction and oxidation half reactions are separated in space and can only run when they are connected by an electrical circuit.

- But we have so many different electrical needs in the modern world. Our cars need a quick, powerful jolt of electricity to start their gasoline engines. Many simple tools require a long and steady current delivery. Portable electronics need power sources that are not only light and small, but also can be recharged over and over again.

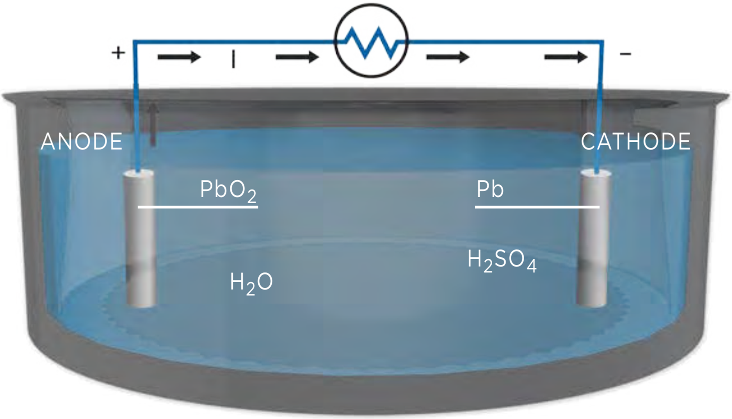
- With so many different needs to be met, can chemists and engineers deliver products that accomplish all of the needed goals? So far, they have—and it has led to the creation of a number of electrical battery technologies that many people take for granted today, but that required decades, or even centuries, of careful research and testing to perfect.

LEAD-ACID BATTERIES

- Automobiles have a long and influential history. The earliest prototypes of what can truly be thought of as automobiles were crafted in the late 1700s. In France, a scientific powerhouse at that time, a man named Nicolas-Joseph Cugnot created a steam-powered vehicle for the purpose of transporting cannons across the battlefield for the French army. He proved that locomotion of such a vehicle was possible without the use of a beast of burden.

- For nearly a century after Cugnot's invention, many other ingenious people lent their talents to the design of machines intended to make our lives easier by moving people and products from one point to another. A contest of the minds ensued over exactly how to power vehicles.

- Cugnot's steam design was refined by others as the decades and centuries passed. Automobiles with electric power and combustion engines eventually entered the race for dominance on the roads of America and Europe. Ultimately, it was the gasoline engine that took hold in the late 1900s. But ironically, one of the devices that brought gasoline powered vehicles to the forefront was an electrical device.



- Gasoline engines need to be cranked to start. The piston must cycle a few times under the force of another device before the engine will cycle on its own. This was a real sticking point in the early 1900s, as gasoline-powered vehicles required an operator to get out, walk to the front, and wind a spring-loaded crank to provide the energy to start the engine.

- But what if a gadget could be used to do the work of cranking up the engine at the push of a button or the turn of a key? This became possible when the electric starter motor was developed and paired with one of the most influential battery designs of all time: the lead-acid battery.

- The foundations of that shift were laid nearly a half century earlier in 1859, when a Frenchman named Gaston Planté built the first lead-acid battery. It looked different than modern versions. Planté simply took 2 sheets of lead, placed a cloth between them, and rolled them into a spiral. This spiral was placed into a jar of dilute sulfuric acid, and each sheet of lead was connected to a wire.

- But this seems a bit unintuitive. Voltaic piles worked specifically because the 2 electrodes supported different half reactions. Planté's design, with identical lead electrodes, wouldn't produce any voltage. Planté's battery was not ingenious because it could create electricity like a voltaic pile, but rather because it could be charged using an external voltage and then discharged at will.

- By placing a voltage across the electrodes, initially hydrogen was formed at the cathode and oxygen at the anode. The oxygen could then react with the lead sheet at the anode, forming lead oxide. Hydrogen, on the other hand, did not react with lead at the cathode and simply escaped.

- With a lead-oxide plate for one electrode and pure lead for the other, we have all the makings of a battery: a cathode, an anode, and a medium for the transmission of ions.

- A so-called lead-acid battery generates current using 2 redox half reactions: the reaction between lead oxide and the acid that's in the electrolyte of the battery; and the reduction half reaction. The summation of these 2 reactions gives us the overall cell potential.

- This gives us a very easy way to construct batteries that deliver voltages in multiples of 2. We simply wire the appropriate number of compartments in serial to get the total voltage that we want.

- Modern versions of Planté's brainchild are often manufactured with a lead-oxide layer preapplied to one of the plates within a cell, eliminating the need for the electrolytic conditioning that Planté relied on to achieve the chemistry he wanted. In most other ways, the sealed batteries that you might buy at the store are made of the same materials that Planté first mixed about a century and a half ago. The robust burst of current, recharge ability, and low cost of these devices make them indispensable to us even now.

ALKALINE BATTERIES

- Planté's lead-acid battery was perfectly suited for the burst of energy needed to start a car, but what about something that needs a bit more sustained energy? Devices such as lamps and music players need more than just a quick electrical shot to operate. They take all of their operating power from electrical batteries. That means a steady, sustained flow of current, which means a steady, sustained voltage.

- But the Nernst equation makes it clear that Planté's device can't do this very well. Cell electromotive force (EMF) is dependent on concentrations, and the acidic electrolyte is actually consumed when a lead-acid battery discharges. That spells trouble because the voltage delivered will change as the battery dies.

- This is frustratingly all too real to anyone who has been stranded with car problems. That ever-slower turnover of the starter, or the slowly dimming headlights, remind us that the voltage supplied by our battery is ebbing away.

- Short of those rare situations in which you are waiting for someone to jump your car, lead-acid does alright for your car. But if we want to use batteries as a portable substitute for a wall outlet, we need something more.

- Enter a completely different design in electrical batteries: the alkaline battery. In the 1950s, a Canadian researcher named Lewis Urry came up with the design of the modern alkaline battery. And although it can be made to look to the end user much like a lead-acid battery, its chemical design is very different.

- With an alkaline battery, the reaction that takes place in the oxidation half reaction is zinc reacting with hydroxide to produce a little bit of water, zinc oxide, 2 electrons, and 1.28 volts of EMF.

- In the reduction compartment of this battery is manganese oxide, reacting to form Mn_20_3, another type of manganese oxide, but one in which it has been reduced, and there's another positive EMF here: 0.15 volts.

- When we put these 2 reactions together, not only do we get a really nice delivery of voltage, but in this particular reaction, there is no liquid, gas, or solution, which means that *Q* from the Nernst equation is effectively 1. In other words, we basically eliminate the issue of nonstandard conditions.

- This allows these batteries to run very smoothly and deliver steady current, with the bonus that they aren't liquid, so we don't have to worry about spilling their contents when they're turned over. This so-called dry-cell battery chemistry has gone on to become the alkaline batteries of today.

LITHIUM-ION BATTERIES

- In the early 1990s, a new technology was made mainstream when it was adopted by Sony Corporation and integrated into many of its electronic devices, especially the mobile ones. The lithium-ion battery was heralded as a breakthrough in battery technology.

- Light, powerful, and rechargeable, this battery technology is part of many of the devices that we have come to find indispensable. Cell phones, portable computers, and in some cases automobiles and medical equipment all rely on the lithium-ion battery.

- Credit for its design often goes to John Goodenough, who developed some of the very specialized materials that are needed to produce these brilliant devices. This invention brought battery technology into the 21st century at a time when it was sorely needed. Computing power and portable computing devices were gaining in popularity and affordability at that time, and one of the most significantly lagging technologies holding these devices back was their power needs.

- This newer battery design has several immediate advantages over its predecessors.
  - Each cell produces 3.7 volts of potential, about 3 times the potential of a traditional alkaline battery.

  - The design is extremely robust and can be easily recharged hundreds or thousands of times without significant loss of storage capacity.

  - As the lithium ion battery has been advanced over the years, new electrolyte materials have made it one of the lightest battery options on the market.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 877–888.
Knight, *Humphrey Davy*.
Masterton and Hurley, *Chemistry*, 18.5.
Pancaldi, *Volta*.

QUESTIONS

1 The voltages needed to power electric cars (a few hundred volts) can easily be obtained by wiring modern battery cells in series to create something similar to the piles used by Alessandro Volta and Humphrey Davy. If the appropriate voltages are so easily attained, then what are some of the challenges associated with designing battery systems for vehicles?

2 Imagine that you are Humphrey Davy using a voltaic pile to isolate potassium metal from the potassium ions in lye. Knowing that the reduction potential for potassium ions to potassium metal is –2.92 volts, how many cells must your voltaic pile have to accomplish this task (i.e., make the reduction of potassium spontaneous)?

Answer

2) To push the reaction forward, the voltaic pile must provide enough voltage to overcome the reduction potential of the potassium metal. Four cells would be needed to achieve the necessary voltage. (0.76 volts per cell × 4 cells = 3.04 volts.)

Nuclear Chemistry and Radiation

LECTURE 43

Although chemical bonds can be used to store and release massive amounts of energy, the energy involved in the making and breaking of chemical bonds pales in comparison to the energy that holds nuclei together. This energy, known as the nuclear binding energy, powers nuclear reactors, weapons of mass destruction, and even our Sun. Instead of focusing on building up compounds by bonding atoms together, this leg of your journey is dedicated to better understanding building up and breaking down the atomic nucleus by adding and removing subatomic particles. In this lecture, you will learn about nuclear chemistry and radiation.

STRUCTURE OF THE ATOMIC NUCLEUS

› Atoms are composed of a dense, central nucleus that is made from protons and neutrons—particles that are collectively called nucleons. The protons give the element its identity. For example, 2 protons in the nucleus means that you are dealing with helium, regardless of how many neutrons are present.

› The neutrons give the nucleus additional mass without changing the identity of the element. So, helium with one neutron has a total atomic mass of 3, while helium atoms with 2 neutrons have a mass of 4.

› These 2 atoms are called isotopes. In this case, both are stable, and both are found in nature, although helium-4 atoms are much more abundant, comprising all but about one in a million helium atoms.

- This relationship extends to all other elements. For example, carbon-12 and carbon-13 are both found in nature. Each has 6 protons, making them both carbon nuclei, but carbon-12 has only 6 neutrons, while carbon-13 has 7.

- Even larger elements, such as uranium, have multiple isotopes. Uranium-235 has 92 protons and 143 neutrons, while uranium-238 has 92 protons and 146 neutrons. Both are uranium nuclei and will bond and behave chemically in very similar ways. But when we step down to the level of nuclear changes, these 2 uranium atoms behave very differently.

- To distinguish isotopes, nuclear chemists write their elemental symbols with 2 numerical notations preceding them: one at the top of the element's symbol and one at the bottom of the symbol. The top number indicates the total mass of the nucleus, and the lower number indicates the number of protons.

$$^{238}_{92}\text{U}$$

RADIOACTIVE DECAY

- In 1895, German physicist Wilhelm Roentgen discovered that by passing electrical current through a coil inside of a very powerful vacuum, he could create a type of electromagnetic radiation that could expose photographic film and penetrate many different materials that ordinary light did not.

CROOKES TUBE

Roentgen discovered X-rays by using a Crookes tube like the one pictured here.

- Uncertain of what to call this radiation, but equally certain that it was a groundbreaking observation worthy of reporting to the scientific community immediately, Roentgen dubbed his new discovery “X-rays.”

- The following year, a French physicist named Henri Becquerel was conducting experiments with uranium-containing compounds. He had been exposing these compounds to light, then placing them in a darkened room and exposing them to photographic paper in an attempt to prove a theory that X-rays were reemitted sunlight somehow changed by the uranium.

- It is an interesting theory, but one that was undone by a cloudy day. When Becquerel had no Sun available to expose his uranium one day, he conducted a control experiment, removing the Sun from the equation and exposing the photographic paper to his uranium compound anyway.

- To his surprise, the film still showed evidence of exposure. His theory was crushed, but his place in history was secured by this observation. Becquerel had shown that the radiation was the result of some intrinsic process within the uranium nucleus, not the reemission of stored energy from elsewhere. Uranium atoms had the ability to emit some sort of radiation on their own. Radioactivity had been discovered.

- In fact, the radiation that he discovered was not X-ray radiation. He knew this because he discovered that passing a beam of his newly discovered radiation through an electromagnetic field caused the beam to bend into 2, as though some of the particles making it up were positively charged and others were negatively charged.

- Once he had this realization, Becquerel used his technique to discover that many different materials had this ability to emit beams of particles that could expose photographic paper. In addition, some emissions were positively charged, some were negatively charged, and some were not charged at all.

- Some materials emitted only one of these beams, while others emitted some or even all of them. Clearly, there was a process fundamentally based on the atomic structure of these elements that determined how they decayed and which types of radiation they produced.

NUCLEAR DECAY REACTIONS

- We now know that what Becquerel had discovered in his earliest experiment was not electromagnetic radiation, but a radioactive decay product—small pieces of the uranium nucleus that had been ejected from the nucleus as it reordered itself into a different, more stable arrangement.

- What exactly were the 3 types of radiation that were observed in Becquerel's experiments? The answer to that question would take some time, but clues were offered in the experiments of Ernest Rutherford, most famous for his model of the atom, who noted that the radiation beams observed in Becquerel's apparatus had not only differing charges, but varying ability to penetrate aluminum.

- Rutherford repeated Becquerel's experiments but successively placed layers of aluminum foil into the apparatus between the uranium radiation source and the photographic paper, acting as a detector. When he did this, he observed that the positively charged radiation did not penetrate the foil as well as the negatively charged radiation, and neither of those could match up to the penetrating power of the uncharged radiation.

- Rutherford named the positively charged radiation alpha radiation and the negatively charged radiation beta radiation. The third type of uncharged radiation is called gamma radiation.

- In addition to alpha, beta, and gamma decays, there are many other players in the process of nuclear decay. Two common processes are electron capture and positron emission. By these processes, protons can convert into neutrons, altering the identity of elements and even turning hydrogen atoms into bare neutrons, the likes of which make up neutron stars.

- Alpha radiation is made up of helium-4 nuclei. Beta radiation is made up of high-energy electrons ejected not from the cloud around an atom, but from the atom's nucleus itself. Gamma radiation is high-energy electromagnetic radiation resulting from transitions in the structure of the nucleus itself as it relaxes after a nuclear reaction.

- Electrons and positrons are nearly massless compared to nucleons, so losing or even gaining one does not change the mass of a nucleus, but it does change that nuclei's identity, effectively adding or removing a proton depending on the process, promoting a rearrangement in the nucleus that can emit powerful gamma radiation.

- Electron capture is the process that takes place in the formation of neutron stars. As large dying stars collapse, pressure increases in the core of these stars. The pressure can become so high that protons themselves collapse, capturing their orbiting electron and becoming a neutron instead. With no electron cloud, neutrons have a much smaller radius than hydrogen atoms do, explaining how neutron stars can achieve their densities of about 100 trillion times that of the Earth.

NUCLEAR STABILITY

- Why do some atomic nuclei decay or transform over time while others do not? Atomic nuclei are very challenging structures to understand. With all of the electrostatic repulsion going on between and among positive charges in the confined space of an atomic nucleus, how do they stay together at all?

- The answer to this question is as fundamental as it is elusive. No one really knows exactly why, but there are a few general trends in the stability of nuclei based on the number of protons and neutrons that it contains.

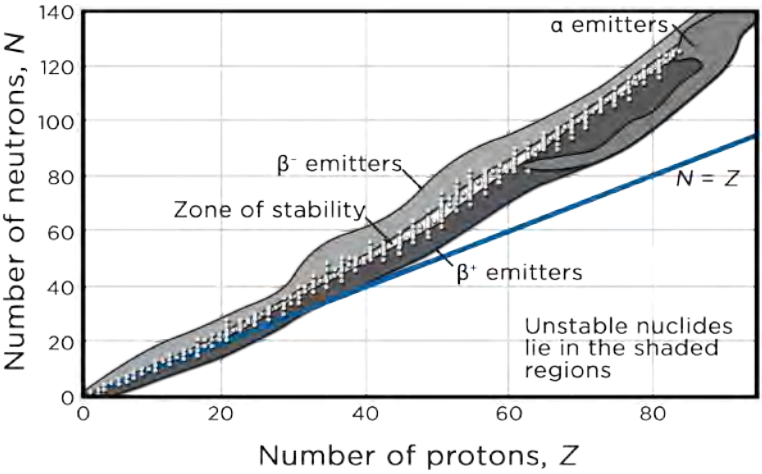
- In general, nuclei with 2, 8, 20, 28, 50, or 82 protons tend to be more stable. The same numbers apply to neutrons, with 2, 8, 20, 28, 50, 82, or 126 neutrons being more stable.

- There also is a strong tendency for there to be an even number of protons, neutrons, or both in stable elements. Of all known stable isotopes, more than half have an even number of both protons and neutrons. Possibly more surprisingly, only 5 of 265 known stable isotopes have an odd number of both protons and neutrons.

- This information isn't enough to crack the code of how nuclear structure affects stability, but it is more than enough to compel us to the assumption that nuclear structure does matter. Having even numbers of nucleons imparts stability somehow.

- There are also other trends in stability. Consider a chart with the number of protons on the *x*-axis and the number of neutrons on the *y*-axis. As stable isotopes become larger, their ratio of neutrons to protons grows predictably, creating a curved region of the plot commonly known as the zone of stability. This gives us a cursory tool for the prediction of how a given unstable nucleus might decay.

- For example, nuclei above the zone of stability can move toward the zone by emission of a beta particle, stepping from left to right on the diagram toward the optimal ratio.



- In contrast, isotopes below the zone of stability need to increase their neutron-to-proton ratio. This can be accomplished by positron emission or electron capture. One very common example of this is the element fluorine-18, which decays primarily by positron emission.

- Elements larger than lead have no stable nuclei, and their quest to lose mass will often lead to the emission of alpha particles. A great example of this is the decay of uranium-238, which undergoes not just one, but 8 different alpha decays on its way to becoming lead-206, squarely in the zone of stability.

USES OF RADIOACTIVE DECAY

- Radiation exposure has a potentially toxic effect. It is widely believed to have been the culprit behind an early demise for many great scientists who made some of the first discoveries in this field, such as Marie Curie. In addition, adverse health impacts can be caused by overexposure to radiation from reactor meltdowns and nuclear weapons fallout.

- But radioactivity isn't all bad. Shortly after its discovery, Bertram Boltwood used it to estimate the age of the Earth, launching a quest to understand how our solar system and galaxies formed. And some keen minds, such as Curie's, quickly realized that the high-energy content of radiation might make it dangerous in high, uncontrolled doses but might also make it a useful medical tool when properly harnessed. In fact, Curie is widely recognized as the world's first radiation oncologist, because she realized that directed radiation could be used to kill cancer cells in humans.

- Clever use of radioactive nuclei has led to the development of certain cancer therapies. In addition to using radiation in medical therapies to kill localized cancer cells, the high-energy particles that it can create and its ability to change the very identity of the element emitting it can be used in a number of positive ways, including in the medical technology known as positron-emission tomography (PET) scanning, which is very useful in the detection of certain cancers.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 902–915.
Masterton and Hurley, *Chemistry*, 19.1.

QUESTIONS

1 Alpha particles are much less dangerous than gamma radiation when encountered from the outside of our bodies. However, alpha particles can be one of the deadliest types of radiation when ingested. Why is this so?

2 Beryllium-8 is a remarkable isotope because it is by far the smallest nucleus that can undergo an alpha decay. Write the nuclear reaction for this process and explain why beryllium-8 is the smallest nucleus capable of this kind of radiation. Explain why some believe that this process should not be considered a classical example of nuclear radiation.

Answer

2) ${}^{8}_{4}\mathrm{Be} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{4}_{2}\mathrm{He}$.

Beryllium-8 breaks into 2 alpha particles, leaving no daughter nucleus behind.

Binding Energy and the Mass Defect

LECTURE 44

Your investigation of nuclear chemistry has covered most of the processes by which atoms can radioactively decay as a means of reaching a more stable state, but you have not yet considered the energetics of those processes in a quantitative way. This will be remedied in this lecture as some numbers are put to the incredible forces involved in holding the atomic nucleus together. You will discover why so little nuclear material can pack such tremendous energy.

THE MASS-ENERGY RELATIONSHIP

- For so long, matter and energy were very conveniently divorced in the minds of physicists—at least, that assumption was widely applied. But even as early as 1717, the undisputed father of modern physics, Isaac Newton, questioned that principle when he considered the possibility that light and matter could be interconverted.

- For so many years, though, the laws of conservation of mass and conservation of energy held fast in the face of scientific scrutiny. The only way it seemed that energy could be stored and released was in the breaking and making of chemical bonds. Atoms, at least until the days of Becquerel and Rutherford, appeared to be indestructible, indivisible objects.

- But that began to change when Becquerel first observed the effects of radiation in his uranium samples. Rutherford and others continued refining our understanding of the structure of the atom and the origins of radiation until a grand realization was made by one of the greatest physicists of all time, Albert Einstein.

- In 1905, Einstein published a paper in which he famously shattered the old paradigm that matter and energy were disparate. He did this by offering a mathematical relationship that quantified what Newton had suspected almost 200 years earlier.

- This mathematical relationship is known as his mass-energy relationship. In short, he proved that matter and energy were not separate entities, but could be interconverted. In other words, matter can be turned into energy, and vice versa.

- His equation was almost mind-bogglingly simple, relating the mass of an object to the energy it can be converted into by just a single proportionality constant: the square of the speed of light. This equation, $E = mc^2$, has become the most iconic physical equation of all time—not only because it is so easy to remember, but also because it represents a fundamental shift in the way that humans looked at the universe.

- That fundamental shift in thinking involved just how much energy can be stored in and retrieved from matter. In just 1 gram of matter, you could extract billions of calories of energy. Specifically, you could extract 9×10^{13} joules, or 2.15×10^{10} kilocalories, of energy.

- Einstein's mass-energy relationship gives us not only a way to relate mass to energy, but also a new respect for the almost-incomprehensible amount of energy that is available to be tapped if we can control that interconversion.

NUCLEAR BINDING ENERGY AND THE MASS DEFECT

- It's difficult to believe that you could extract billions of calories of energy from just 1 gram of matter, because we have no way of completely converting a sample of matter into energy. That kind of wholesale interchange simply is not achievable under any kind of conditions that we can even imagine, let alone create.

- Why, then, was the mass-energy relationship such a big deal? The answer to that question is nuclear chemistry. Einstein's equation doesn't just explain a hopelessly theoretical situation; it also explains a very observable, and very useful, phenomenon that we see in atoms called the mass defect.

- J. J. Thomson, who is revered for his discovery of the electron, was able to estimate the mass of an electron by deflecting it in an electrical or magnetic field as it moved through one of his famous cathode-ray tubes. That was a brilliant concept, and one that he continued to develop.

- Thomson used a similar strategy to devise an instrument that could be used to measure the mass of practically anything with a charge. His new creation was called a mass spectrometer, and it worked on principles similar to his cathode-ray tube.

- Just as before, he used an evacuated tube containing a cathode and anode. But this time, he elongated the tube behind the cathode and found that a positively charged beam was moving in the opposite direction from the cathode rays. He named these positively charged beams canal rays.

- Thomson placed a photographic plate behind this new, positively charged beam and was stunned by what he saw: When an electrostatic or magnetic field was applied across the canal rays, they fanned out into an array of beams, each with a different curvature, all of which were much less than the curvature of the cathode ray.

- After a bit of calculation, Thomson realized that the various beams in the canal ray were actually cations—positively charged ions—of carbon, oxygen, hydrogen, and other atoms forming in response to the opposing flow of electrons.

- He named his apparatus a mass spectrometer. Thomson spent a great deal of his career refining his design in the hopes that his strategy of deflecting canal rays might lead to a technique for determining the mass of atoms and molecules with greater accuracy.

- True to Thomson's vision, mass spectrometers improved in their precision and accuracy. Soon, they yielded the masses of various atoms with truly stunning resolution. Throughout the early 1900s, as mass spectrometry techniques improved and our understanding of atomic structure evolved, scientists began to notice a very interesting trend.

- Protons and neutrons make up nearly all of the mass of an atom. They are collectively called nucleons and are packed together in the nucleus of the atom. So, it stands to reason that if we know the mass of a proton and the mass of a neutron, we should be able to calculate the mass of any nucleus simply by accounting for all of the nucleons and adding up their masses.

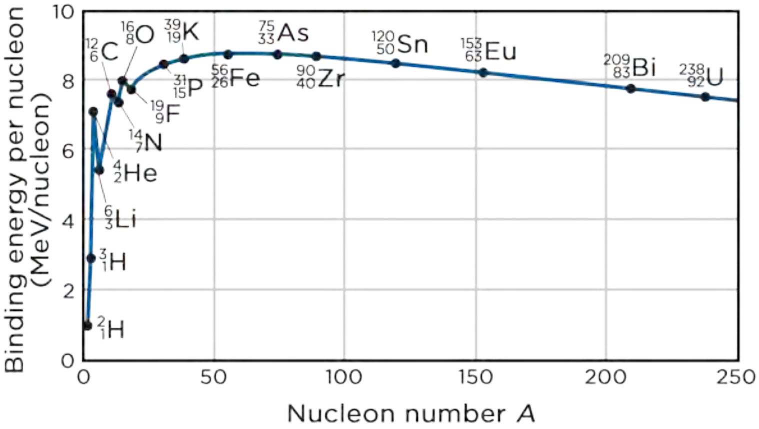
- Scientists were able to use very sophisticated versions of the mass spectrometer invented by J. J. Thompson to measure the exact mass of not only nuclei, but nucleons as well. We benefited from those measurements in terms of being able to calculate a mass defect.

- A mass defect is simply calculated by taking the theoretical mass and subtracting from the actual, or measured, mass. The balance tells us how much mass is released in the form of energy when we create a helium-4 nucleus from its components, nucleons.

- From the mass defect, we can determine the nuclear binding energy, or the total amount of energy when helium-4 is released, formed from its constituent nucleons. Using Einstein's equation, the energy is equal to the mass defect times the speed of light squared.

- If we want to compare the overall stability of one nucleus or another, however, we can't simply use the overall nuclear binding energy. We have to normalize the binding energy to the number of nucleons present. When we do this, we notice a very interesting trend in the values that we obtain.

- This curve of nuclear binding energies, devised by Francis Aston while he was working in J. J. Thomson's laboratory, tells an amazing story of how and why some of the most powerful energy-emitting processes in the universe take place.



- It explains so much about what we see in the universe. Notice that binding energy spikes dramatically for helium atoms, explaining why they form so readily, both as the by-product of our Sun's furnace and as alpha particles in radioactive decay.

- Iron also has a particularly special place on the table. Notice that iron-56 is the king of all nuclei when it comes to binding energy. To separate a nucleus of iron-56 into its constituent parts requires more energy than any other nucleus. It is this remarkable stability of iron that makes it so common in our universe compared to most other metals.

- We can very generally say that all nuclei aspire to be iron. So, heavier atoms, such as uranium and beyond, tend to be radioactive because the process of shedding alpha and beta particles successively can give them a pathway to becoming a lighter, more stable element with a higher nuclear binding energy than the original.

- Iron-rich meteorites and planetary cores are no accident. They are out there, or down there, because under the hot, high-pressure conditions of supernovae, iron nuclei form in large amounts and then are ejected into space as the collapsing star that formed them explodes in a violent supernova, seeding the universe with the nuclei that it helped to create.

- So, the mass defect is directly proportional to the binding energy holding the nucleus together, but we have no real chance of ever converting an atom completely into energy—this is something that even a supermassive star cannot accomplish. Even so, both nature and humanity have been able to tap the nuclear binding energy with amazing results.

MASS DEFECT AND RADIATION

- How do the measured nuclear binding energies explain Becquerel's observations that uranium-238 emits alpha particles?

- Let's look at a problem that involves radiation and see if we can explain why alpha particles seem to form so easily from uranium-238.

- Using the masses provided, estimate how much mass energy is released in the alpha decay of a single uranium-238 nucleus.

$$^{238}_{92}\mathrm{U} \longrightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\alpha$$

- Uranium-238, containing 92 protons and a total of 238 nucleons, will decay into an alpha particle to the helium nucleus, leaving behind 90 protons to make thorium, with a mass of 234.

- If we measure the actual nuclear masses of these 3 species, we find that the mass of uranium is 238.05078825 atomic mass units, thorium is 234.04360123 atomic mass units, and helium is 4.00260325 atomic mass units. These are staggering resolutions, but we need them because we are dealing with such small changes in mass when it comes to mass defects.

- How can we determine the mass defect of this overall process? We essentially rely on a version of Hess's law. We add the masses of the products together and subtract that number from the mass of the reactant to determine the difference for the reaction.

mass = 238.05078825 amu

$$\boxed{^{238}_{92}\mathrm{U}} \longrightarrow \boxed{^{234}_{90}\mathrm{Th}} + \boxed{^{4}_{2}\alpha}$$

mass = 4.00260325 amu

mass = 234.04360123 amu

$$\begin{array}{rr} & 234.04360123 \text{ amu} \\ & 4.00260325 \text{ amu} \\ \underset{-}{+} & 238.05078825 \text{ amu} \\ \hline \Delta\text{mass} = & 0.00458377 \text{ amu} \end{array}$$

- When we add the observed mass of thorium and alpha particles and subtract that number from the mass of the uranium, we discover that the difference is 0.00458377 atomic mass units—a vanishingly small fraction of the mass of a uranium atom.

- If the uranium atom is going to undergo this decay, it's obviously going to reach a lower energy state, because we found that the change in mass is positive. Let's use that number to determine what kind of energy we're dealing with.

- We go back to Einstein's equation, with a slight variation: $\Delta E = \Delta mc^2$. We use the delta symbol (Δ) in front of energy and mass to indicate that we're dealing with the mass defect for a process, comparing one to the other. This is the total change in mass for the system, which will allow us to calculate how the energy of the system changes using the mass defect.

$$\Delta E = \Delta mc^2$$

$$\Delta E = 0.00458377 \cancel{\text{amu}} \left(\frac{1.6606 \times 10^{-27} \text{ kg}}{1 \cancel{\text{amu}}} \right) (3.00 \times 10^{8} \text{ m/s})^2$$

$$\boxed{\Delta E = 6.85 \times 10^{-13} \text{ J}}$$

- After converting atomic mass units into joules and inserting the speed of light squared (3×10^8 meters per second squared) into the equation, we get an answer of 6.85×10^{-13} joules.

- If we use Planck's constant and the equation that relates the energy in a photon to its wavelength, we discover that this type of energy corresponds to the energy of a gamma ray photon.

- We not only showed why alpha emission occurs, but we also succeeded in proving that it should also have a gamma emission associated with it, which is exactly what was observed by Rutherford, Becquerel, and their colleagues.

- Lowering the per-nucleon binding energy is the driving force behind the radioactivity of uranium and other heavy elements like it.

MASS DEFECT AND CHEMICAL BONDING

- With all this talk about nuclear binding energies and mass defect that occurs when multiple nucleons come together to form a nucleus, you might wonder whether chemical bonding creates a similar mass defect.

- The unfortunate truth is that we simply can't measure any such defect if it exists, even with modern equipment. This is because the energy changes in the breaking of chemical bonds is so small compared to that of nuclear binding energies.

- We already have a sound understanding of how the forming and breaking of chemical bonds releases and absorbs energy. Maybe someday we will have instrumentation so sensitive that we can answer the question of whether or not chemical bonding includes a mass defect, but for now, we simply don't know.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 916–920.
Masterton and Hurley, *Chemistry*, 19.3.

QUESTIONS

1. If iron-56 is the most stable nucleus, having the highest per-nucleon nuclear binding energy, then why are many lighter elements, such as hydrogen and helium, much more abundant in our universe?

2. Plutonium-238 decays slowly (half-life of 87 years) and releases a tremendous amount of heat, primarily by alpha emission. What is the product of this alpha decay?

Answer
2) uranium-234.

Breaking Things Down: Nuclear Fission

LECTURE 45

In this lecture, you will learn about the process of nuclear fission. You will also consider nuclear chain reactions and how the by-products of nuclear fission processes can go on to initiate other fission events. Additionally, you will discover how the fission chain reaction can be used to produce reliable power from uranium taken from the Earth. Furthermore, you will learn what can happen when power plants experience reactor meltdowns. Finally, you will explore how nuclear fission was used to create the most destructive weapon ever deployed to the battlefield by our species: the atomic bomb.

NUCLEAR FISSION AND CHAIN REACTIONS

- Although alpha, beta, and gamma radiation are all by far the most common decay processes that elements like uranium take to reach more stable states, they are not the only ones, especially when the nucleus is a little bit less stable than normal.

- Isotope uranium-235 makes up a very small percentage of naturally occurring uranium—less than 1%—but it has something that uranium-238 does not: the ability to break into 2 nuclei of nearly equal size. When nuclei can break into 2 pieces, both larger than an alpha particle, they are fissile, which means breakable.

- One of the reactions that uranium-235 can undergo spontaneously is a fission reaction in which it brakes apart into 2 larger nuclei: a barium-141 and a krypton-92. And to maintain that mass balance, 2 neutrons (which we would call radiation) are going to result from this process.

$$^{8}_{4}\mathrm{Be} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{4}_{2}\mathrm{He}$$

- The fact that 2 large nuclei—much larger than any alpha particle—resulted, this is called a fission reaction. Specifically, we call this a spontaneous fission reaction, because the uranium-235 will do this all on its own without any kind of perturbation. It will happen slowly, over very long periods of time, but it will happen spontaneously.

- This is one of the primary ways, but only one of many ways, that uranium-235 can break apart into 2 smaller nuclei. In truth, when uranium-235 breaks down, it produces a series of nuclear reactions, all of which release energy and produce new elements.

- Let's focus on just the dominant, primary reaction taking place. The fission reaction of uranium-235 and the energy that it releases make it a remarkably useful atom. Part of what makes this and other fissile nuclei so different from those like uranium-238 that only undergo simple, steady radioactive decay is that fissile nuclei can often be made to undergo fission either very rapidly or very slowly.

- The radioactive decay of elements is a first-order process and occurs at a fixed rate that can never be changed. It is so predictable and unchanging that radioactive decay is the basis for radiological dating methods. But the fission of uranium-235 nuclei can be made to happen slowly enough to supply power for electrical needs for years or to be over in less than 1 millionth of 1 second, causing an explosion the likes of which humanity has never seen. Why?

- In the early 1940s, Enrico Fermi discovered that unlike radioactive decay, which relies simply on the statistical likelihood that a nucleus will spontaneously eject an alpha, beta, or gamma particle in a given amount of time, nuclear fission of uranium can be induced by the collision of a neutron with the uranium-235 nucleus. And the reaction itself produces 2 neutrons.

- When a neutron that is generated in the spontaneous fission of uranium-235 collides with yet another nucleolus of uranium-235, this collision is called induced nuclear fission. In this reaction, we have a neutron as one of the reagents. The neutron is going to come from outside and collide with the uranium-235 nucleus, which initiates another fission. The neutron collides, creating the fission by-products, but it also creates 2 new neutrons and the original neutron. This means that 3 neutrons are created for every collision.

$${}_{0}^{1}\mathrm{n} + {}_{92}^{235}\mathrm{U} \longrightarrow {}_{56}^{141}\mathrm{Ba} + {}_{36}^{92}\mathrm{Kr} + 3\,{}_{0}^{1}\mathrm{n}$$

- These neutrons could potentially induce additional fission reactions to take place in other uranium-235 nuclei if they're present. The result is a nuclear chain reaction, in which one fission begets more fission, which begets even more fission. Very quickly, a relatively large population of neutrons can be built up, flying around inside a sample, colliding with new uranium-235 nuclei, and promoting more and more of these reactions to take place.

- The concentration of neutrons flying around in a sample containing uranium-235 directly affects how rapidly the sample will undergo fission. This concentration of free neutrons in a sample of material is called neutron flux. Because the fission of uranium-235 is a second-order process overall, the fission of uranium-235 can be accelerated or decelerated by controlling the neutron flux.

- Fissile nuclei break only when a neutron hits them. Neutrons can be coaxed to release their energy more slowly if we can keep the number of triggering projectiles—neutrons—down to a minimum or by spacing out the reactive nuclei so that they are farther away from one another.

- Fermi was confident that he had this all worked out—so confident, in fact, that he built a demonstration of it under the University of Chicago. He piled uranium and graphite in a large spherical-shaped arrangement—not within tons of concrete, not cordoned off by barriers of lead, but in the open, in a tennis court under the west-viewing stands of the abandoned Stagg Field at the university.

- At 3:25 pm on December 2, 1942, Fermi's pile went critical and began producing his chain reaction, which sustained for 28 minutes. He had proven his point. He had risked countless lives, including his own, in the process, but he had proven his point: A sustainable chain reaction could be created and controlled.

- Inside a nuclear reactor, the neutron count is kept down using rods made of neutron-absorbing materials, such as indium or cadmium; rods of this kind of material can be lowered into the nuclear fuel to decrease available neutrons or raised to allow more neutrons to continue in the reaction.

- Using this technique and a fuel made from uranium as it is recovered from ore—meaning just about 0.7% uranium-235—can sustain a controlled nuclear fission reaction for about 6 years with a little bit of human help.

NUCLEAR REACTORS AND MELTDOWN

- Nuclear reactors were a brilliant invention. They use low concentrations of uranium-235, so they cannot create a nuclear explosion even under the worst-imaginable conditions. But they are not without risk.

- Most nuclear power plants are actually sophisticated steam generators. A reactor core containing the nuclear fuel is used to generate heat. This heat is often used to generate steam, which turns turbines to create electricity.

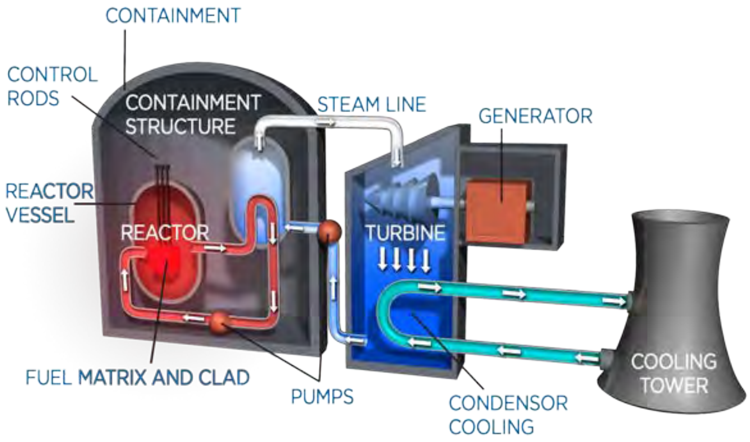
- Because the uranium-235 abundance in the fuel is low, a nuclear explosion is impossible. But the temperatures that can be generated by a runaway reactor are so high that a host of other catastrophes can happen when things get out of hand.

- One of the more famous examples of this is the Three Mile Island accident, which happened on March 28, 1979, in Pennsylvania. During this incident, a valve intended to release steam from the water-cooling system stuck open, allowing most of the water coolant to escape.

- As the core temperature rose, operators tried to lower control rods into the fuel to slow the reaction by absorbing neutrons to reduce the neutron flux. But it was too late. The heat from the runaway reaction had so badly warped the core that the rods would not fit into their receivers properly.

- The reactor was doomed. As the temperature inside soared, the reactor itself melted into a puddle of nuclear material at the bottom of the core. Fortunately, the core walls withstood the stratospheric temperatures and no nuclear material escaped.

- This is in contrast to the infamous Chernobyl accident, in which the plant operators and the people of Chernobyl in Ukraine were not so lucky. A steam explosion contributed to a reactor breach at this plant in 1986, throwing fuel and its radioactive by-products into the air and the surrounding area, scarring the town to the point of uninhabitability.



FISSION BOMBS

- Fermi's experiment under the University of Chicago in 1942 heralded a new age for humanity. He had demonstrated that man could control the nuclear fission reaction and harness it as an engineering tool. In the case of Fermi's pile, the goal was to create a self-sustaining nuclear chain reaction that could deliver continuous energy over long periods of time.

- And it did so, providing an early blueprint not just for Three Mile Island and Chernobyl, but for the many dozens of nuclear plants that have performed safely over the decades since they were designed and built.

- But this was all just a by-product of the true goal. Fermi's work was funded by the famous Manhattan Project, an effort by the U.S. government to harness the power of nuclear fission for a very different application.

- Fermi's design was intended to run slowly. He used natural-abundance uranium samples, in which uranium-235 atoms are diluted by their much more stable uranium-238 siblings. He also used neutron-absorbing graphite to slow down the chain reaction in those uranium-235 atoms, sustained when neutron by-products of their fission strike other uranium-235 atoms, perpetuating the process.

- But the real goal on everyone's mind was not to create a sustained fission reaction, but a violent one. Fermi's design allowed scientists to study the nuclear fission reaction closely and relatively safely, but research on nuclear fission continued. It was wartime, and the ultimate goal of the Manhattan Project was to create a weapon that could dispense all of that nuclear binding energy in an instant.

- The first nuclear weapons developed by humankind all relied on the nuclear fission reaction to work. They are based on the same principles as Fermi's stack, but with a few design changes to make the chain reaction deliberately run away as fast as possible.

- The 2 most infamous nuclear weapons in history—the only 2 ever actually used in war—were products of the Manhattan Project: Little Boy and Fat Man.

- Little Boy used the exact same reaction as Fermi's reactor at Chicago. But to get the reaction to run away, there needed to be much more neutron flux than in Fermi's reactor. So, instead of using control rods to reduce the density of fission-inducing neutrons, the facility at Oak Ridge National Laboratory, a school of reactor technology in Tennessee, spent huge quantities of time and energy to enrich uranium-235 beyond its natural abundance of 0.7% to 80%. This hundredfold increase in abundance ensured that there would be plenty of neutrons rattling around in the bomb's payload, making that sample potentially explosive.

- The next thing that was needed to produce a nuclear explosion was what is known as a critical mass of fissile material. In the case of the uranium-235 used in Little Boy, this mass was about equal to the weight of an ordinary human being.

- When the size of the nuclear material meets or exceeds critical mass, the neutron flux in the center of the mass is sufficient to start a runaway chain reaction that releases the nuclear binding energy in an instant, creating the massive explosions and accompanying mushroom clouds that we are accustomed to seeing in historical films and photographs.

- Little Boy was dropped over the Japanese city of Hiroshima on August 6, 1945, releasing a blast that leveled an area 1 mile across. Fat Man was deployed to the city of Nagasaki 3 days after Little Boy, causing similar devastation. Thankfully, in the 70 years since, an explosion of such magnitude has never been used in a wartime theater.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 920–924.
Cobb and Goldwhite, *Creations of Fire*, pp. 391–409.
Masterton and Hurley, *Chemistry*, 19.4.
Stein and Powers, *The Energy Problem*, pp. 143–153.

QUESTIONS

1 In this lecture, fission was presented as a 1-step process in which a single nucleus splits into 2. Can more complex fission take place, producing 3 or more nuclei in a single process?

2 Although fission is usually associated with heavy elements, a few examples of light elements undergoing fission do exist. Lithium-7, for example, can be used to produce tritium (hydrogen-3) and one additional product by fission. Write a nuclear reaction and determine what the other product of this fission is.

Answer

2) ${}^{7}_{3}\mathrm{Li} \longrightarrow {}^{3}_{1}\mathrm{H} + {}^{4}_{2}\mathrm{He}$.

An alpha particle is the other product of this nuclear reaction.

Building Things Up: Nuclear Fusion

LECTURE 46

You already learned how large nuclei break down to form smaller ones in a quest to become smaller, more stable nuclei with greater binding energies per nucleon. But if heavier elements tend to break down to lower their energy, then smaller ones, such as hydrogen and helium, should want to come together to create larger elements. Chemists call this process nuclear fusion. Although there are other nuclear fusion reactions, this lecture is dedicated to the fusion of hydrogen atoms to make helium.

NUCLEAR FUSION

- Nuclear fusion reactions are the alter ego of fission reactions. They involve the building up of large nuclei from smaller ones. In most cases, taking 2 smaller elements and combining them together to make a larger one is an energetically beneficial proposition.

- But there is a catch. How do you get 2 atoms to combine with one another? That is asking a lot. As 2 nuclei approach one another, there is a natural repulsion due to the charge on their nuclei. This force is called coulombic repulsion, and to overcome this repulsion and induce 2 nuclei to come close enough to potentially combine requires more than a small amount of force.

- This is why stars are so critical to the elemental diversity of the universe. Stars like our Sun are the only place in nature that temperatures and pressures are adequate to induce the fusion of atomic nuclei to form new elements. Without stars, our universe would consist of nothing more than hydrogen, helium, and maybe a smattering of lithium.

- Fortunately for us, there are supermassive stars across the cosmos that have burned for billions of years, smashing atoms together into ever-larger elements before exploding in giant, forceful supernovae, seeding the universe with heavy elements.

- Although fusion can theoretically occur between just about any 2 atoms when conditions are right, the simplest and most powerful nuclear fusion reaction is the fusion of hydrogen atoms to make helium. This reaction has fueled our Sun for 5 billion years and likely will for at least another 5 billion.

- Something as simple as the fusion of 4 hydrogen nuclei into a helium atom has created and will create essentially all of the energy that our planet will ever receive from outside. This energy will be released over billions of years, during which the Sun will convert just a miniscule fraction of its mass into energy.

- The whole story of the Sun's machinery is much more complicated, but from an energetics standpoint, the fusion of hydrogen to helium is the 800-pound gorilla. Many other nuclear reactions can take place, creating heavier elements up to and including iron, but the primary driver of the Sun's furnace is indisputably this remarkably simple nuclear reaction.

FUSION AND THE H-BOMB

- The fusion of nuclei is not relegated to processes in deep space, though. Human engineers and scientists have discovered ways to harness fusion reactions like those that take place in the Sun. The most recognizable of these is what is commonly known as the hydrogen bomb, a device created not long after the historic bombings of Hiroshima and Nagasaki. Those bombs used a very different nuclear reaction.

- The so-called H-bomb finds its roots in a question that Enrico Fermi posed to another researcher on the Manhattan Project, Edward Teller, in 1941. By then, the design for the gun-type and implosion-type fission devices were well worked out. Even though none had been constructed to that point, confidence was high that the devices would work and generate kiloton yields.

- But Fermi thought that he could do better, using what is a fairly logical progression. If conventional explosives could compress and heat fissile material to the point of a fission explosion, yielding kilotons of force, could a fission reaction create the truly awesome pressures and temperatures needed to produce a nuclear fusion reaction in a weapon that would tap the raw power of the Sun itself?

- It is a great idea on paper, and Fermi and Teller worked on the idea until the end of the Manhattan Project in 1946. At that point, World War II was over, and the Manhattan project disbanded with its mission accomplished.

- But Teller harbored a deep distrust of the Soviets and, even as early as the 1940s, expressed his concerns passionately and publicly. Teller remained driven by what he and many others could sense was coming, a protracted power struggle among the victors of World War II, and he believed that superior armament was one of the keys to protecting America's interests.

- So, Teller continued his research with all the fervor that he had when preparing the fission weapons during the Manhattan Project. He would not rest until a weapon based on nuclear fusion was developed.

- Let's consider some of the reactions that go on inside the Sun that Teller hoped to emulate in his new weapon. We always think of nuclear fusion going on in the Sun as hydrogen being fused to make helium, but there are actually quite a number of ways to do this.

- The simplest is to take 4 of those hydrogen atoms and mash them together to create a helium nucleus and 2 positrons in the process. If we take these protons and have them collide, overcoming coulombic repulsion, we still have to get rid of 2 units of positive charge to make a helium nucleus.

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{1}\mathrm{p}$$

- This is one of the nuclear reactions that goes on inside the Sun. The problem with trying to set up a reaction like this on Earth is that you can't reach the kinds of pressures and temperatures necessary, even if you're going to use a nuclear bomb as your blasting cap. This type of reaction doesn't take place at any kind of condition that we could ever hope to generate, even with the deadliest and most powerful nuclear bombs.

- There are other nuclear reactions going on in the Sun. For example, instead of fusing the 4 protons all at once, in a collision of 4 different species—which is very rare and very unlikely to have happened—let's fuse them to make 2 deuterium molecules. This is 2 binary collisions, instead of a single collision of 4. This still gives us positron emission, but it leads us to having deuterium as one of the intermediates in the process.

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow 2\,{}^{2}_{1}\mathrm{D} + 2\,{}^{0}_{1}\mathrm{p} \longrightarrow {}^{4}_{2}\mathrm{He}$$

- Another binary collision of those 2 deuterium molecules can take place, which will give us helium-4, which the Sun is always after making, and release a tremendous amount of energy as nuclear binding energy. This gives the Sun a work-around to getting over the fact that it's trying to have a quaternary collision. A series of binary collisions is much easier to accomplish at high pressures and temperatures.

$$2\,{}^{2}_{1}\mathrm{D} \longrightarrow {}^{4}_{2}\mathrm{He}$$

- Teller wanted to use one of these reactions to release energy in the form of a weapon. He had the option, potentially, of using deuterium. If he were to have fused deuterium into helium, he would get helium and a lot of energy, just like the Sun.

- But there's a problem: the amount of energy required to overcome the coulombic repulsion. Deuterium can be made to fuse into helium, but it requires temperatures in the tens of millions of kelvins, and that is too hot to generate, even using nuclear bombs in his day.

- Instead, Teller turned to a third reaction that goes on inside the Sun, one involving the other isotope of hydrogen: tritium, which is a little bit more massive than deuterium. This means that it has a little bit more momentum and is able to overcome the coulombic repulsion better when it approaches a deuterium nucleus.

$$ {}_{1}^{2}\mathrm{D} + {}_{1}^{3}\mathrm{T} \longrightarrow {}_{2}^{4}\mathrm{He} + {}_{0}^{1}\mathrm{n} $$

- Teller could fuse a tritium and deuterium much more easily. It takes about a million, or a few million, kelvins to do this, and in the process, it releases a neutron as a bonus. Not only does it lower the necessary temperatures to the point at which they can actually be created by a nuclear bomb, but it also releases a neutron, which can convert yet another deuterium into tritium, which can perpetuate the reaction. This is the reaction that Teller used to create the now-famous hydrogen bomb.

- Teller's research demonstrated that a reaction like this could be used in a weapon capable of producing explosive yields that would make Little Boy look like a firecracker.

- He proposed a weapon in which a primary fission explosion created sufficient heat and pressure to begin the reaction. It forced a plutonium rod into a liquid helium fuel source at temperatures in excess of 4 million kelvins—all to turn deuterium into helium.

- The first such device that Teller and his colleagues ultimately helped create was codenamed Ivy Mike, and it was built on the remote island of Elugelab in the Marshall Islands of the South Pacific. In 1952, the Ivy Mike device was detonated, and the power of the stars was unleashed by humans for the first time. After the 10-megaton explosion, the island of Elugelab was gone, replaced by a crater.

- Engineering developments eventually led to the development of deployable weapons of even greater power, none of which, thankfully, have ever been used.

CONTROLLED NUCLEAR FUSION

- It took until 1920, and the discovery of the mass defect of helium, for scientists to finally have the idea that the fusion of hydrogen might be something that could be achieved on Earth.

- It took several decades yet again, and the advent of the Manhattan project and others like it, for humans to finally create a fusion reaction of their own. The first of these were explosive devices like Ivy Mike, with uncontrolled fusion being the goal.

- But can nuclear fusion be not only initiated, but controlled? Could we somehow tap this incredibly powerful reaction the way that Fermi did with fission? It is a tantalizing prospect.

- Just imagine if we could tap nuclear fusion in a controlled way—not using fission bombs to initiate fusion reactions that are over in less than a second, but a more elegantly conducted reaction, in which hydrogen isotopes are fused into helium and the energy of that process is tapped.

- We would have power plants that use the most abundant element in the universe as fuel and produce harmless, stable helium as waste that simply floats into space.

- But the problem is that even deuterium-tritium fusion, which is the easiest fusion reaction to start, requires temperatures of about 40 million kelvins to sustain. The energy needed to overcome the coulombic repulsion of 2 hydrogen nuclei is so monstrous that we can't run fusion in a power plant the way that we do in a bomb.

- There must be something fundamentally different about how a fusion reactor is designed if it is going to be practical for power generation. We have to find a way to run the same nuclear fusion reaction at drastically lower temperatures—to create a type of "cold fusion."

- The quest for controlled nuclear fusion started at about the same time that thermonuclear weapon research began. Attempts to use magnetic fields to create containment systems capable of generating high pressures have been employed. Physicists call this the pinch technique.

- Although many of these types of systems have been able to contain high-energy hydrogen isotopes, none can create conditions right for nuclear fusion. But that doesn't mean that humankind will never find a way to harness this awesome reaction.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 924–925.
Cobb and Goldwhite, *Creations of Fire*, pp. 409–414.
Masterton and Hurley, *Chemistry*, 19.5.
Stein and Powers, *The Energy Problem*, pp. 153–157.

QUESTIONS

1. Do you believe that controlled nuclear fusion will be achieved in your lifetime?

2. The superheavy element copernicium was first synthesized in 1996 by firing high-speed zinc-70 atoms at a lead-208 target. The 2 atoms fused and produced a single free neutron in the process. What is the atomic number of copernicium, and which isotope was synthesized in this landmark experiment?

Answer

2) Copernicium's atomic number is 112.
Copernicium-277 was formed in the reaction.

Introduction to Organic Chemistry

LECTURE 47

Carbon is one of the simplest of all the elements. At element number 6 on the periodic table, it is a relatively small atom in size, but this small element holds a crucial place in the workings of the universe and, particularly, of life. The term “organic” refers to molecules with carbon-based structures, and organic chemistry is the study of carbon and carbon-containing compounds, which are found in living things. This lecture will dive into organic chemistry by exploring hydrocarbons.

CARBON

- Why is carbon used as the backbone or scaffold of so many small molecules that drive living systems? What makes carbon so special?
  - Carbon is relatively abundant. It is difficult to estimate exactly how much carbon is available at or near the surface of the Earth, but it is undeniable that it is concentrated there.

  - Carbon is stable when bonded to itself. Carbon bonds to itself with great strength, requiring about 400 kilojoules of energy to break a mole of bonds. That’s more energy than most bonds would need to break. This means that carbon skeletons are sturdy. They can support other structures that can undergo reactions to perform their functions.

  - Carbon is able to form complex chains of atoms. To create a biosphere with such tremendous diversity, nature needed a large library of compounds. Carbon is perfectly suited as a scaffold to build this library because its $1s^2\ 2s^2\ 2p^2$ electron configuration allows it to make up to 4 bonds in a tetrahedral arrangement. Because of this, chains of carbon can extend, branch, and even fold back on themselves. In doing so, they create enormously complex structures, all of which have even more unsatisfied bonds to which a variety of atoms can be attached.

- When you compare these 3 properties of carbon, nothing else on the periodic table can compete. Among the elements, just a few have the abundance to even be considered to serve as a molecular scaffold. Among the few elements abundant enough to be in the running, none can beat carbon in the necessary categories. Carbon-based molecules offer more variety, stability, and functionality than any other possibility.

HYDROGEN

- The most abundant element in the universe, hydrogen falls short in our test for a good backbone element because it can only form one bond to complete its valence electron shell. Although hydrogen would be a lousy backbone choice, its ability to make only one bond does have use.

- Hydrogen atoms bond strongly to carbon, but only to one carbon. This makes a carbon-hydrogen bond a perfect way to terminate a chain of carbon atoms. So, hydrogen behaves much like a placeholder in this respect.

HYDROCARBONS

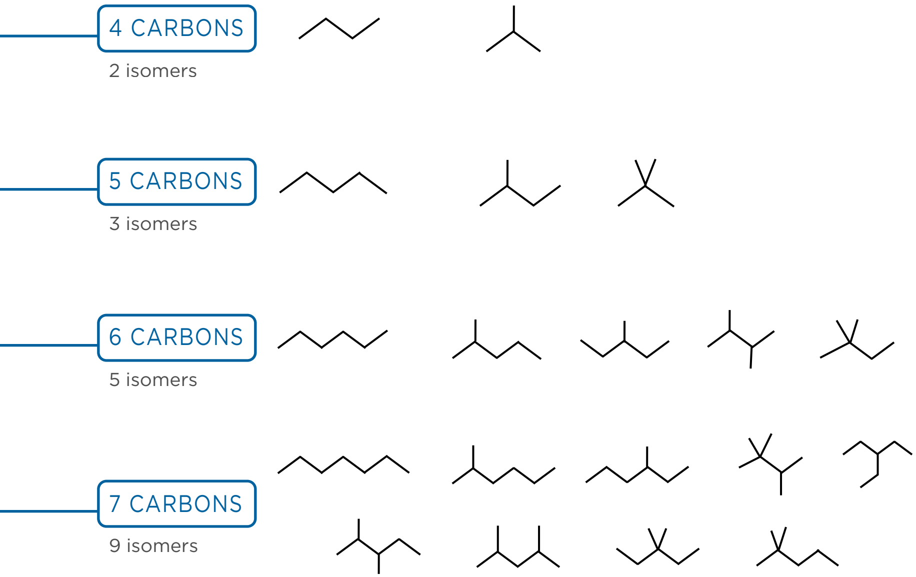
- When we combine just these 2 elements, hydrogen and carbon, we get a class of organic compounds called hydrocarbons, which are the principal component of a number of motor fuels—from natural gas to gasoline to kerosene. All of these vital products consist of very little more than hydrogen and carbon.

- But hydrocarbons have many other uses. For example, benzene finds use as an industrial solvent, and the gas ethylene is used in plants to signal that it is time for fruit to ripen. Hydrocarbons, though representing just a small slice of carbon-based molecules, have a very rich and complex chemistry.

- A skeletal formula is a type of notation that makes it easier to draw complex structures. Each of the ends of the lines represents a carbon atom. Every kink in the line also represents a carbon atom.

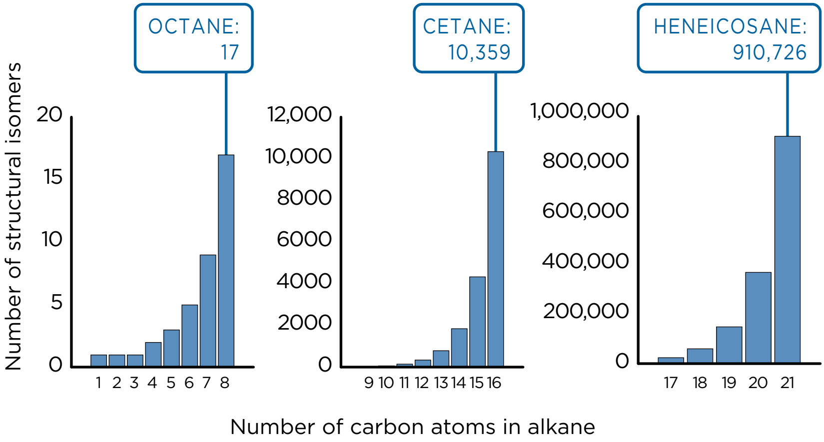
- The total number of possible saturated hydrocarbons—that is, those that only have single bonds—that contain 4 carbons is 2. In other words, there are 2 potential isomers. In the case of having 5 carbons, there are 3 different ways to connect those 5 carbons into geometrically distinct configurations, or isomers. With 6 carbons, we can make 5 isomers. And there are 9 different ways can we put 7 carbon atoms together into either a chain or a branch structure.

ISOMERS OF HYDROCARBONS



- As we add additional carbon atoms, we increase the potential variety. And this increase is not linear—it's exponential.

- Consider a plot of all the potential numbers of isomers of hydrocarbons that contain up to 21 carbon atoms. If we go up to 21, we're dealing with possibilities that are approaching the millions.



- When we put all of these possibilities together, it creates a library of more than a million hydrocarbon structures. And when we consider double and even triple bonds being in these molecules, the number of possibilities becomes virtually infinite.

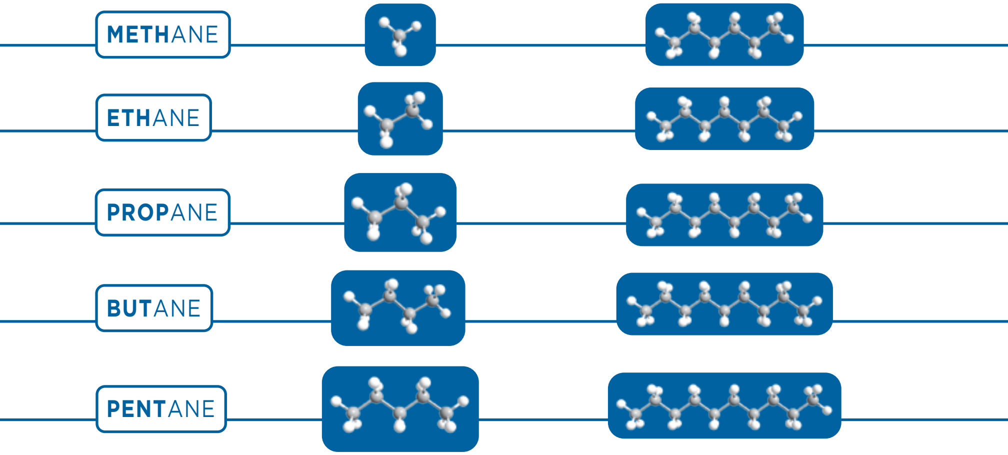
NAMING HYDROCARBONS

- There are millions upon millions of unique molecular structures for hydrocarbons. Learning a common name for each one would be virtually impossible. Luckily, we have a much more manageable way to talk about hydrocarbons, courtesy of the International Union of Pure and Applied Chemistry (IUPAC). IUPAC oversees and recommends naming conventions so that instead of having to memorize millions of unique names, we can instead memorize just a few simple rules that are used to construct them.

- Let's begin our inquiry into how to name saturated hydrocarbons by thinking about the number of carbons in the molecule. We'll start with some very simple hydrocarbons. Methane, ethane, propane, and butane are names for hydrocarbons that contain 1, 2, 3, and 4 carbon atoms, respectively. These prefixes ("meth-," "eth-," "prop-," and "but-") come from generally historical sources; they're not terribly methodical.

- Fortunately, scientists eventually came to their senses, and as we begin adding more and more carbons beyond 4, we see more familiar prefixes in pentane ("pent-") with 5, hexane ("hex-") with 6, heptane ("hept-") with 7, octane ("oct-") with 8, nonane ("non-,") with 9, and decane ("dec-") with 10. This trend continues, using the appropriate prefix for the appropriate number of carbons.

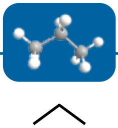
NAMING HYDROCARBONS



- This system of naming is incomplete. It only allows us to determine how many carbon atoms are within the molecules, and there is a tremendous amount of variety in terms of isomers. Although this nomenclature system gets started on distinguishing what kind of hydrocarbon we're talking about, it doesn't complete the picture.

- To complete the picture, we have to think more about how these molecules can branch. In the case of propane, there really isn't any branching to worry about. You can't have a branch with just 3 atoms. The skeletal structure of propane will always be similar no matter what.

PROPANE

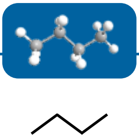


propane

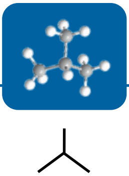
- In contrast, there are 2 common names for the 2 potential isomers of butane. The first molecule is labeled *n*-butane. The *n* at the beginning stands for "normal," which is the generic nomenclature term that lets us know that all the carbons are in a continuous straight chain. This is an example of a skeletal structure of *n*-butane.

- However, we can branch a butane molecule. We need a new name that allows people to know which one of these 2 isomers we're talking about. We call this particular structure isobutane.

BUTANE

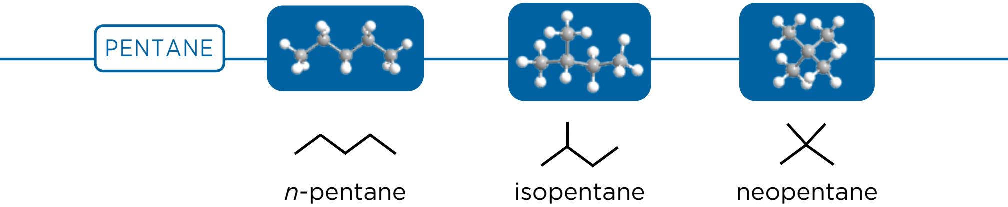


n-butane



isobutane

- Pentane can branch in several different ways. It can branch with one carbon in the branch, giving us what we would call isopentane, or it can be even more highly branched, creating a structure that is known as neopentane.



- As we go on and on in the number of carbons, we're going to start running out of prefixes to use—or, at the very least, the mental capacity to memorize all of them. We certainly couldn't memorize more than a million potential names for a million potential hydrocarbons from one to 21 carbons. We use the IUPAC nomenclature system when it comes to naming hydrocarbons.

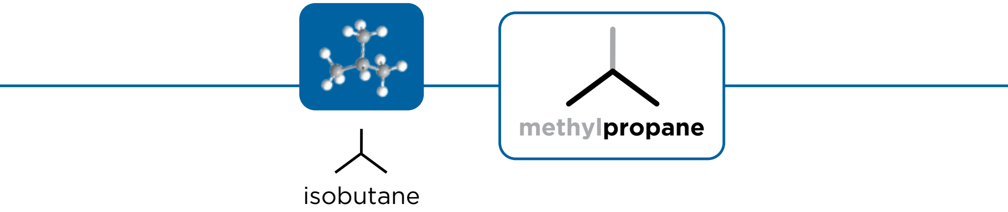
- The IUPAC nomenclature system for saturated hydrocarbons is fairly simple. We just follow 4 rules:
  1. Identify the parent hydrocarbon, which means finding the longest string of carbon atoms that you possibly can.
  2. Catalog all of the alkyl substituents that are on those particular parent hydrocarbon molecules: methyls, ethyls, propyls, etc.
  3. Assign a numerical address along that parent hydrocarbon so that we can indicate the locations of all of the substituents that we identified in step 2.
  4. Construct the name using a set of simple rules.

- For example, let's assign IUPAC names to isobutane, isopentane, and neopentane. Starting with isobutane, how many carbons are in the longest chain of this molecule? There are 3.

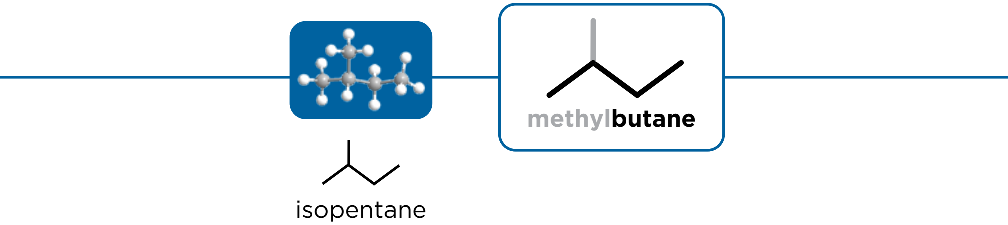
- What are the substituents? There is one carbon off the chain. Because the prefix for one carbon is "meth-," we will call this a methyl substituent.

- In the case of isobutane, there's no need for an address because there's only one potential location for the split to be.

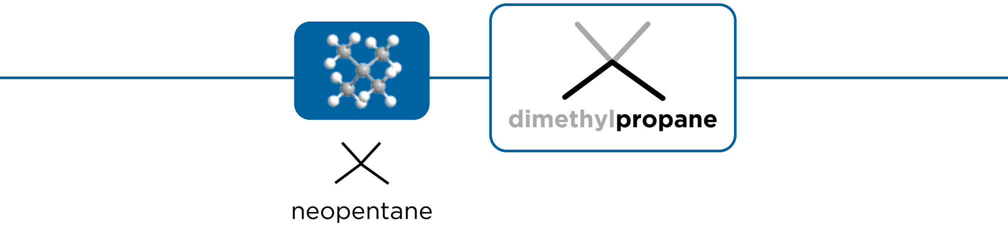
- Isobutane, by common nomenclature, is methylpropane in IUPAC nomenclature, because common nomenclature considers the total number of carbon atoms in the name, whereas IUPAC considers only the length of the parent chain when it comes to the root of the name.



- Isopentane is called methylbutane in IUPAC nomenclature.

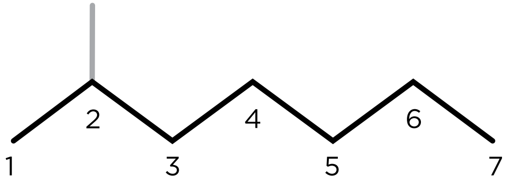


- Neopentane is called dimethylpropane in IUPAC nomenclature because the longest carbon chain is only 3 atoms, and there are 2 methyl substituents.



- So far, we haven't had to worry about where the substituents were on the parent chain because the parent chain was so small that there was only one potential location, but there are potential situations in which that's not true.

- How can we name the following molecule using IUPAC conventions?



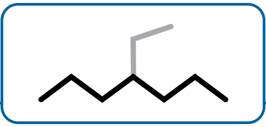
- We have to define the parent hydrocarbon and the substituents. The parent hydrocarbon is black, while the one methyl substituent is gray. Before we can finish the naming process, we have to know exactly where the methyl group is. We can assign a numerical address to the parent hydrocarbon.

- Because the IUPAC nomenclature system requires that we give the lowest possible address number to the substituents, we start numbering with a 1 at the left end of the molecule and go along sequentially until we reach 7 at the right end. In this case, the methyl group receives a number of 2.

- If we were to number this chain in the other direction, the methyl group would receive a number of 6, which is higher than 2 and therefore is not preferred in the IUPAC system. A methyl group at position 2 on a 7-carbon chain is named 2-methylheptane.

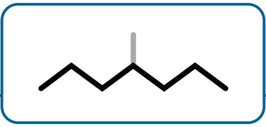
- Other examples of hydrocarbons are as follows:

4-ethylheptane

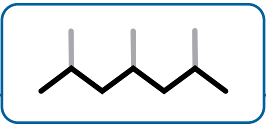


2-methyloctane

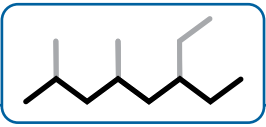
4-methylheptane



2,4,6-trimethylheptane



6-ethyl-2,4-dimethyloctane



- This should give you all of the information you need to name just about any simple saturated hydrocarbon that you might encounter.

- Although compositionally very similar, hydrocarbons can be structurally very diverse. As diverse as they are, they also share quite a few properties in common. Hydrocarbons are almost uniformly combustible and insoluble in water.

- But their volatility in particular can vary dramatically. Chemists and engineers can exploit the differences in volatility of hydrocarbons to separate them from one another using a modern version of the ancient technique of distillation.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 1064–1074.
Masterton and Hurley, *Chemistry*, 22.1–22.3.

QUESTIONS

1. Hydrocarbons can be linear and branched but can also take on cyclic forms, in which the carbon chain turns back on itself, forming a loop. How might you name such compounds if you were IUPAC?

2. Distillation is not only useful for isolating water from salts or hydrocarbons from one another. What other uses has distillation found over the years?

Heteroatoms and Functional Groups

LECTURE 48

There is much more to the world of organic chemistry than just hydrocarbons. Just about every element in the periodic table can play a part in the chemistry of carbon-based compounds, but in this lecture, you will learn about halogens, oxygen, and nitrogen and the roles that they can play in tuning the chemistry of organic compounds. In the process, you will develop an appreciation for the structural complexity of organic compounds and how those structures can affect their physical properties.

HETEROATOMS

- When any element other than carbon and hydrogen is present in an organic compound, these new additions are called heteroatoms. The inclusion of heteroatoms has a few very special effects on organic compounds.

- First, the inclusion of more electronegative elements—such as nitrogen, oxygen, fluorine, and chlorine—can introduce bond-level dipoles into molecules, creating classes of compounds that contain polar bonds. The presence of these polar bonds can have dramatic impacts on the physical properties of a compound by introducing the possibility of molecular polarity, varying levels of acidity, and even hydrogen bonding.

- Second, more complex geometries and even more isomers become possible, because heteroatoms like nitrogen and oxygen can not only replace hydrogen atoms in hydrocarbon frameworks, but also extend and sometimes even branch chains themselves.

- These 2 factors in combination create a truly massive library of remarkably diverse compounds—one that dwarfs even the staggering inventory of possible hydrocarbon structures, both in size and complexity. Indeed, the inclusion of heteroatoms into the discussion gives us a virtually endless supply of potential compounds to study.

HALOGENS IN ORGANIC CHEMISTRY

- Halogens, like hydrogen, typically form only one bond, capping off one bond in a carbon scaffold. When we replace one or more hydrogens with a halogen, the new molecule is called an alkyl halide—"alkyl' for the alkane we started from and "halide" to indicate that at least one halogen has replaced a hydrogen.

- Rigorously, in organic chemistry, the halide on an alkyl halide is often called a substituent rather than a functional group. IUPAC nomenclature treats halogens just like alkyl groups, so when naming alkyl halides by this convention, we follow the exact same method that we did in the previous lecture.

- When it comes to alkyl halides, the carbon backbones are essentially unchanged, but halogens are bigger—in some cases much bigger—than the hydrogen atoms that they replace. They are more electronegative, too. This means that when we start replacing hydrogen atoms with halogen atoms, we begin introducing larger electron clouds and some new polar bonds that weren't there before. This can have profound impacts on the physical properties of an organic compound.

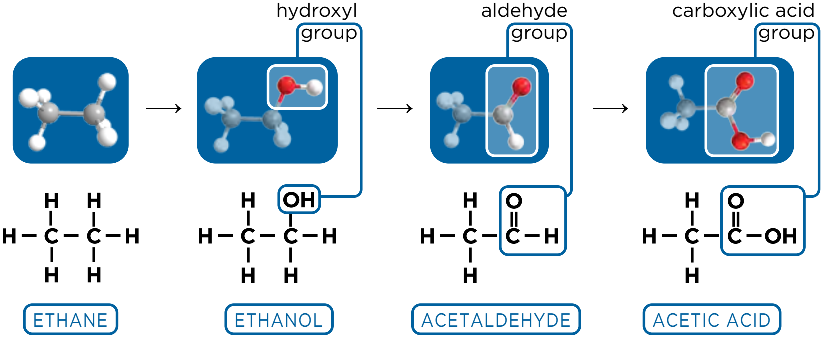
OXYGEN-CONTAINING COMPOUNDS

- Oxygen is a very common element. In its pure, diatomic form, oxygen provides us with a means of tapping energy as bonds of other molecules interconvert via combustion. Your car needs it to burn octane for energy, and your body needs it to oxidize other fuels, such as the sugars, fats, and proteins in the foods that you eat.

- But once it reacts with organic material like hydrocarbons, oxygen isn't done. In a complete combustion reaction, we depict oxygen reacting with a hydrocarbon to become carbon dioxide and water. This is the ultimate product of the reaction, but more controlled oxidation reactions can lead to new organic materials that contain oxygen.

- Let's take the hydrocarbon ethane and add oxygen to it. But instead of doing so as we might in a combustion reaction—where we simply add as much oxygen as we possibly can, essentially obliterating the molecule—let's add that oxygen atom by atom, bond by bond, forming new organic molecules.

OXIDATION OF ETHANE



- In the first step, we add one oxygen to the ethane molecule. The simplest way to do this is by placing the oxygen in a single bond to one of the carbons, and it's also going to need a hydrogen to cap it off. This results in a molecule of ethanol—an alcohol—and the O-H group is called a hydroxyl group.

- We can add additional oxygens, or additional bonds to oxygen, in several ways, the first of which is we simply create a double bond to the oxygen. We have to remove 2 atoms of hydrogen from the molecule to do this, but we add a new connection to the oxygen, so we would say that this is more oxidized. This molecule is known as acetaldehyde, and it contains what we call an aldehyde group, which is a carbon double bonded to an oxygen and also singly bonded to a hydrogen.

- We still have additional unused connectivities to put oxygen on the molecule. When we put another oxygen on, we add a new hydroxyl, creating an overall group known as a carboxylic acid group. Because the hydrogen in the hydroxyl group is fairly acidic, it's removed somewhat easily.

- But we've added yet another oxygen atom, and yet another bond to an oxygen atom, so we would say that ethane can be oxidized into ethanol, which can be further oxidized to create acetaldehyde, which can be even further oxidized to create the carboxylic acid acetic acid, also known as vinegar. As we add additional carbon atoms to the molecules, things become even more complicated, and we can illustrate this by adding just one more carbon to the equation.

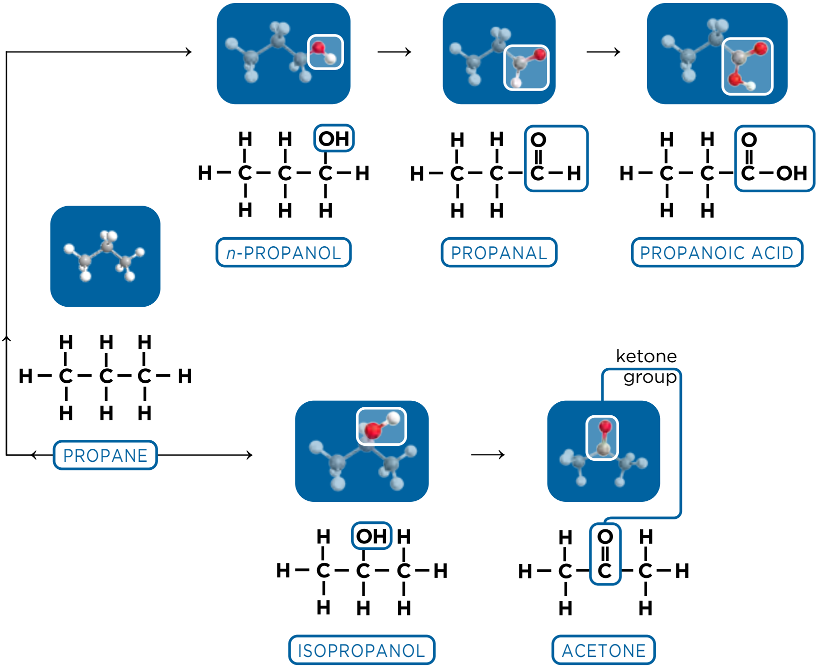
- When we oxidize a molecule of propane, we have to ask a new question: Which one of the carbons gets oxidized? There is a terminal carbon, but there is also a carbon in the middle that's bonded to 2 other carbons and therefore is in a distinct chemical environment.

- So, when we oxidize propane to make propanol, there are 2 possibilities: *n*-propanol (or "normal" propanol), in which the hydroxyl is on the end carbon; or isopropanol (meaning "same as propanol" because they are isomers of one another), in which the hydroxyl is on the central carbon.

- Whether we put the carbonyl on the end or in the center makes a very important difference chemically. When the carbonyl is on the end, we call this propanal, which is an aldehyde; when we put it in the center, and the carbon that is double bonded to oxygen has 2 other carbons, we call this acetone.

- Further oxidation of propanal leads us to propanoic acid, another organic acid, just like we had when we oxidized ethane. This highlights one of the important differences between propanal, which is an aldehyde, and

OXIDATION OF PROPANE



acetone, which is a ketone molecule: We cannot oxidize acetone any further because the carbon is not connected to any hydrogens that we can remove to accommodate a new hydroxyl group. So, the end of the oxidative chain, when we're working with the central carbon, is acetone, whereas the end of the oxidative chain when working with a carbon on the end of the molecule is a carboxylic acid.

- Again, when we oxidize propane, we have to consider where to put the hydroxyl, to get *n*-propanol or isopropanol, and at that point, where to put the carbonyl, the double-bonded oxygen? Do we get propanal, an aldehyde? Or do we get acetone, a ketone? Finally, if we're dealing with a terminal carbon, we can take one more oxidative step to get propanoic acid, a carboxylic acid molecule.

NITROGEN-CONTAINING COMPOUNDS

- Making up 78% of our atmosphere, nitrogen is all around us in its pure, molecular form. It also makes up about 3% of the mass of your body. That might not sound like much, but the role played by that nitrogen cannot be duplicated by any other element in the universe. Many of the nitrogen-containing compounds in our bodies are very large, complex biomolecules, such as the proteins making up your muscles and the wide variety of enzymes catalyzing reactions in your body that are keeping you alive.

- Nitrogen has certain similarities with oxygen. It is relatively small, somewhat electronegative, and fairly abundant in our environment. But it also has some distinctions. Most notably, it readily forms 3 bonds per nitrogen atom, compared to oxygen's 2. This gives nitrogen the ability to form a much broader array of possible bonding arrangements.

- Nitrogen is extremely abundant and totally essential to life as we know it, but it can be difficult to come by in a form that organisms can use. Diatomic nitrogen is joined by a triple bond and is very difficult to break apart because that triple bond is very strong. Breaking this bond to get the nitrogen atoms inserted into an organic compound is exceedingly difficult.

- Thankfully, a few very special bacteria have the ability to break molecular nitrogen down, combining it with hydrogen to form the compound ammonia. Nitrogen in ammonia is bonded to 3 different bonding partners, all of which are hydrogen atoms.

- Ammonia is not truly an organic compound by the modern definition, because it has no carbon atoms. But unlike nitrogen gas, which is practically inert, ammonia can react with organic compounds, inserting itself into the realm of organic chemistry and taking on connections to carbon in lieu of hydrogen.

- Chemists can use ammonia as a starting material to create a number of organic compounds, the simplest of which are called amines. Amines consist of a nitrogen atom that is chemically bonded to an R group, or some kind of a carbon-containing organic motif.

- Because nitrogen can have up to 3 different single bonds, we have a situation where we can have compounds that contain nitrogen with one R group, 2 R groups, or even 3 R groups, in which case we call them primary, secondary, and tertiary amines.

STRUCTURE OF AMINES

A PRIMARY AMINE

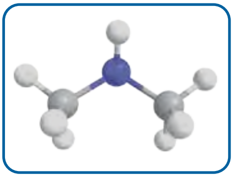
methylamine

CH_3NH_2

A SECONDARY AMINE

dimethylamine

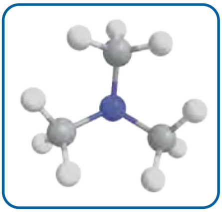
$(CH_3)_2NH$



A TERTIARY AMINE

trimethylamine

$(CH_3)_3N$



- Methylamine has one R group and would be considered primary; dimethylamine has 2 R groups and would be considered secondary; and trimethylamine, which has all 3 bonds to the nitrogen as R groups and none of them as hydrogens, would be called a tertiary amine.

- The number of bonded groups to the nitrogen can have a profound effect on how these compounds behave, both physically and chemically.

- Primary and secondary amines differ from tertiary amines because they have N-H bonds, which allow them to hydrogen bond to one another, raising their boiling point. For example, the primary amine propylamine has a boiling point of about 50°° centigrade, whereas trimethylamine, a tertiary amine, has a boiling point of just 2.9 centigrade. They have the same elemental composition, but very different volatility.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 1082–1091.
Masterton and Hurley, *Chemistry*, 22.4.

QUESTIONS

1 Based on the larger, more-polarizable electron cloud of sulfur, do you expect thiols to be more acidic or less acidic than similar alcohols?

2 Sulfur is too large to form effective pi overlap with carbon to create double bonds. However, it can form single bonds, taking the place of oxygen in alcohols, forming what are known as thiols. What does the Lewis structure of ethanethiol look like?

Answer

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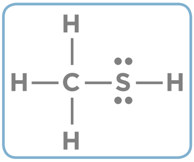


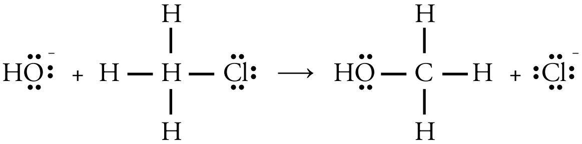
Reactions in Organic Chemistry

LECTURE 49

Organic chemistry is special because it focuses so intensely on organic chemical reactions and how we can use them in a directed fashion to create new and useful compounds. The process of designing and carrying out an organic synthesis reaction can be very complex. This lecture will offer just a small sampling of the factors that go into understanding and using chemical changes in organic molecules. Such factors can effect very specific changes to molecules or groups of molecules, creating all new compounds that can serve a number of versatile roles in our world.

DRAWING ORGANIC MECHANISMS

- Let's consider how bonds might break and form using a relatively simple reaction: the reaction between hydroxide ion and methyl chloride. This reaction is expected to produce alcohol, known as methanol, and a chloride ion.

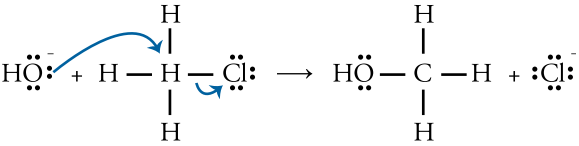


$$\mathrm{H\ddot{\underset{\cdot\cdot}{O}}}\!:^{-} + \mathrm{H}-\overset{\displaystyle\overset{\mathrm{H}}{|}}{\underset{\displaystyle\underset{\mathrm{H}}{|}}{\mathrm{H}}}-\mathrm{\ddot{\underset{\cdot\cdot}{Cl}}}: \longrightarrow \mathrm{H\ddot{\underset{\cdot\cdot}{O}}}-\overset{\displaystyle\overset{\mathrm{H}}{|}}{\underset{\displaystyle\underset{\mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{H} + :\mathrm{\ddot{\underset{\cdot\cdot}{Cl}}}:^{-}$$

- By considering 2 crucial questions—where do electrons want to go, and is there a pathway for them to get there?—we can start to elucidate and even predict how conversions of organic molecules will take place.

- In the reaction, the hydroxide ion is going from an oxygen with 3 lone pairs and a negative charge to an OH, or hydroxyl group, bonded to a carbon. The electrons go from the hydroxide ion to form the new bond to the carbon. In the chloride, the bonding pair of electrons makes its way onto the chlorine atom to make a chloride ion with a full octet, but carrying a negative charge.

- To convey the motion of the electrons, we use curved arrows. Using curved arrows to show the flow of electron pairs allows us to show the chemical change taking place—one that a trained chemist can then reconstruct in his or her mind and begin to understand how electrons and atoms are moving as these reactions are going on.



DESIGNING A SYNTHESIS

- When designing an organic synthesis, researchers have to ask a lot of questions. Naturally, the first question is, what do we want to create? Usually, the structure of a product is predetermined. We know that we want to try a new drug with a methyl group here or a hydroxyl group there.

- So, knowing where we want to go is essential. This usually means carefully drawing out the structure of interest and considering what structural elements it has.

- But knowing our ultimate location isn't the only critical information. We also have to consider where we should begin our synthesis. We have to settle on our starting materials.

- The chain of logic most often used is called retrosynthetic analysis. In this technique, we start from the ultimate goal and ask, from what starting materials can we make this product?

- Next, we go to our lab inventory and look for those materials. If we can't find them, we go back to the drawing board and ask, how can we make those starting materials from other compounds? The process is continued until we find a starting material that is available or on hand and we are ready to head into the lab and run the reaction in the forward direction.

CLASSES OF ORGANIC REACTIONS

- Over the past 2 centuries, scientists have uncovered hundreds if not thousands of types of reactions that can be used to create one organic compound from another. They have learned a tremendous amount about how organic molecules and functional groups can be created, combined, broken down, and interchanged with one another.

- If we want to track how electrons flow when reactions take place, we have to define a few of the players in these general forms of reactions.

- Nucleophiles are defined as species with regions of dense negative charge and lone pair electrons that can be donated to a bond to relieve that charge. Nucleophiles are looking for a positive charge; in other words, they are nucleus-loving—hence the term.

- Conversely, an electrophile is a species with a region of dense positive charge buildup and the ability to receive new electrons to form a bond that relieves that charge. Electrophiles are looking for a negative charge; they are electron-loving.

- Because nucleophiles are out looking for positive charge and electrophiles are looking for negative charge, nucleophiles and electrophiles are looking for each other.

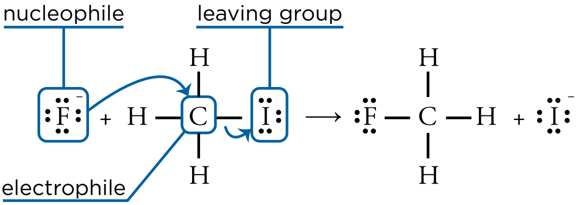
- For example, hydroxide ion would be considered a good nucleophile, because the OH– ion has not only a full unit of negative charge localized on the oxygen, but also plenty of lone pair electrons to use to "attack" an electrophile. An electrophile might be methyl chloride, which contains a polar carbon-chlorine bond.

- In some cases, we will see what are known as leaving groups, which are atoms or groups of atoms that are capable of breaking loose from the electrophile and taking their bonding electrons with them.

SUBSTITUTION REACTIONS

- Organic compounds are built on a stable carbon scaffold that acts as a sort of support for the functional groups that give them their reactivity and properties. When an organic chemist sets out to make a new compound, he or she is rarely forced to start from the beginning. Often, there are available compounds that have the right carbon scaffold but have different functional groups or substituents than the new target product.

- One of the more common substitution reactions that organic chemists use to affect these kinds of changes is what's known as a nucleophilic substitution. An example of a nucleophilic substitution mechanism is one in which a fluoride ion reacts with methyl iodide to displace the iodide ion and create a compound called methyl fluoride.



- The reason that this reaction works is because the electrons from the fluoride ion would rather be involved in a bond than those in the iodide ion that results.

- Why is that so? Isn't fluorine the most electronegative element? The answer to that question is yes, but it's also very small. The negative charge on the fluoride ion is occupied in a relatively small volume. This is a very strong, dense negative charge, whereas the iodide ion has a very large electron cloud and can distribute that charge over it.

- Under appropriate conditions, this transition can be coaxed into happening. When this happens, the fluoride ion is called a nucleophile. That's because the electrons on the fluoride ion want to react with a nucleus. They want to get rid of that negative charge by attacking a nucleus.

- The carbon, or the substrate, that we attacked, is called the electrophile. That's because the carbon is part of a polar bond in which the dipole is pointing toward the iodine. That carbon is already electron deficient and would like to receive those electrons. When the 2 get together, they displace the iodide ion, which is the leaving group. That is more stable than fluoride ion under the conditions that are used for this reaction.

- This simple substitution offers a clear illustration of how electrons might relocate during a reaction to reach a lower energy state. This is where the reactivity of functional groups comes in handy. Their unique reactivity means that they can be targeted and changed when exposed to the right reagents under the right conditions. If we want to place a stronger nucleophile on a location that has a good leaving group, we can use substitution.

ELIMINATION REACTIONS

- Another classic organic reaction mechanism is the elimination reaction, whose name implies that some sort of small by-product is removed from a larger starting material, not unlike a decomposition reaction.

- A very simple example of this is the formation of unsaturated (double- or triple-bond) hydrocarbons from saturated (single-bond) hydrocarbons. Hydrocarbons with a double bond are called alkenes, and those with a triple bond are called alkynes.

- The simplest example of making alkenes is the product of ethylene gas from ethane gas. In the case of this reaction, 1 mole of hydrogen gas is lost for every mole of alkane that is converted into an alkene. This process, called dehydrogenation, takes place at very high temperatures in the presence of special catalysts.

- This is one way that we get ethylene gas. Ethylene is a potent plant hormone that is used to signal fruits that it is time to ripen. It is also a very useful starting material in many organic synthesis reactions, because it contains a pi bond.

- Pi bonds involve electrons held not directly between 2 nuclei, but in the region defined by overlapping *p* orbitals just above and below the internuclear axis. This makes pi bonds somewhat reactive, and their introduction into hydrocarbons can lead to materials at which other reactions can be carried out specifically at the site of the double bond.

- But this simple method of dehydrogenation creates a mixture of unsaturated hydrocarbons that have to be isolated from one another by distillation. All of the carbon atoms in an alkane have carbon-hydrogen bonds that can break to go on to form the product, so one carbon is just about as good as any other.

- This problem can be surmounted using elimination reactions that can be site-directed by using alkyl halides rather than alkanes as starting materials.

ADDITION REACTIONS

- Addition reactions can be thought of as the reverse process of elimination reactions. When pi bonds on a compound are converted into sigma bonds, a great deal of free energy can be liberated because of the reduced enthalpy of the new products created.

- Perhaps the best example of this is the Nobel Prize–winning process developed by French chemist Paul Sabatier in the early part of the 1900s. Sabatier didn't really invent the process of hydrogenation, but some would say that he set us on the path to perfecting it.

- Sabatier used metal catalysts to facilitate the addition reaction, creating a way to more efficiently perform this addition reaction. It wasn't long before his technology was adopted and tuned by chemists trying to find ways to improve the food supply.

- You have probably heard the term "hydrogenated oil." Lately, hydrogenated oil has gotten a fair bit of bad press because we have come to realize the deleterious health effects that it can have. But in the early part of the 1900s, saturated fats were sought-after foodstuffs, primarily because they tend to be solids that can last longer on the shelf.

- The kinds of oils that Sabatier wanted to hydrogenate have a series of double bonds within each of the tails inside the molecule. The goal is to get hydrogen to add to them, but the problem is that hydrogen makes a pretty strong bond to itself and is rather fussy about getting on there.

- Instead of just putting the 2 together and hoping that a reaction will take place, we use a platinum catalyst that weakens the bond between 2 hydrogens and allows a reaction to take place in which the hydrogens add across the double bond, replacing the pi bond between the 2 carbons with new sigma bonds to the hydrogens. This is called a partially hydrogenated oil because we've only added hydrogen to one of the double bonds.

- But organic chemists haven't stopped with simply adding hydrogen. Any number of other elements and groups can be added to molecules using this strategy.

- In certain situations, we need to add new substituents and functional groups to molecules at a specific location, and alkenes give us a way to do this. By starting with the proper alkene, synthetic organic chemists can be sure that the addition of a number of diatomic molecules occurs across a double bond at a specific location.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 52–67, 1004–1006.
Masterton and Hurley, *Chemistry*, 22.6.

QUESTIONS

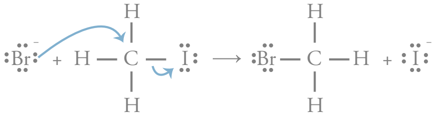
1 Hydrolysis and condensation reactions both take place in your body as your metabolism is carried out. If condensation reactions are taking place and producing water within our bodies, why is it so important that we drink water and stay properly hydrated?

2 Draw the mechanism for a substitution reaction in which a bromide ion attacks methyl iodide to create methyl bromide and an iodide ion.

$$Br^- + CH_3I \rightarrow CH_3Br + I^-$$

Answer

2)



Synthetic Polymers

LECTURE 50

This lecture is all about polymers, which are a class of chemical compounds that you are probably familiar with. The tires on your car, the bulletproof vests protecting soldiers and police, the ropes supporting mountain climbers, and the packaging that protects your food and water from spoilage are all very often made from polymers. Polymers are long series of molecules attached to one another by molecular bonds. The smallest repeating unit of the chain is called a monomer.

LONG CHAINS OR MESSY AGGREGATES?

› What gives trees and lumber their remarkable rigidity to allow them to grow hundreds of feet high in some cases, yet just the right amount of flexibility to weather the most severe storms? Wood has been, and continues to be, a building material of choice all over the world for just these reasons. Live trees, timber, and lumber all share these properties.

› In the 1800s, a French chemist named Anselme Payen is credited with discovering the chemical compound that gives trees and other plants these remarkable properties. Payen isolated a compound that he named cellulose—the "cell-" portion because it is the principal component of plant cell walls and the "-ulose" suffix because it was known to have an empirical formula similar to that of common sugars, whose names bear the same ending.

› But it would take almost 100 years and a ferocious debate for scientists to realize what cellulose really is and how it achieves its incredibly useful properties.

- For many decades, establishment scientists worked with cellulose, natural rubber, and many other tough, useful materials, assuming that they were simply aggregates of small molecules like glucose clinging to one another through exceptionally strong intermolecular forces.

- Then, in 1920, a young upstart chemist named Hermann Staudinger dared to publish a paper offering a new theory. He hypothesized that compounds like rubber and cellulose were not aggregates of small molecules, but instead were monstrously long molecules linked throughout by covalent chemical bonds.

- Staudinger's new hypothesis was brilliant, game changing, and thought provoking—but it was summarily dismissed by Emil Fischer, one of the greatest minds in carbohydrate chemistry in his day. Staudinger vehemently defended his theory against Fischer, a highly regarded chemist who was 30 years his senior.

- It took time to prove, but in 1930, the relatively new technique of X-ray crystallography finally proved Staudinger right. Cellulose was not a disjointed, disordered aggregate of glucose molecules; it is a polymer comprised of long chains of sugar monomers. These long chains are held together by powerful covalent networks that extend for thousands of sugars along any given chain.

- Weave those chains together into a sort of molecular rope held by a massive network of hydrogen bonds made possible by the O-H bonds in the sugar monomers and you have the molecular makings of a material of remarkable toughness and pliability.

NATURALLY OCCURRING POLYMERS

- Confirmation of the structure of cellulose shattered the paradigm that only small molecules existed in our world and showed that Staudinger's macromolecules were real. This changed our thinking about materials and their properties and forced scientists to take a whole new look at some ancient materials that we thought we previously understood.

- Take the example of rubber, or polyisoprene. It is resistant to water because it is a hydrocarbon, but it is amazingly thick and viscous compared to other hydrocarbons. This can all be explained by enormously long hydrocarbon chains composed of polyisoprene sliding along one another, clinging tenuously to one another through van der Waals forces, but bonded within chains by massive networks of covalent bonds hundreds, thousands, or even millions of monomers long.

- The epiphany of macromolecules can also explain the properties of cellulose. Imagine glucose units linked together in chains of thousands. Not only are these individual chains held together by networks of thousands of strong covalent bonds, but multiple chains can interact through hydrogen bonds.

- The covalent networks give it amazing tensile and compressional strength, but the hydrogen bond networks give it just the right shear strength—able to bend, but not break, as a tree in hurricane winds or as a piece of lumber in a settling house.

SYNTHETIC POLYMERS: ADDITION POLYMERS

- Chemists have created polymers from the ground up. There are several ways to classify synthetic polymers. Sometimes we group them based on the chemistry used to create them, and other times we group them by the type and arrangement of monomers.

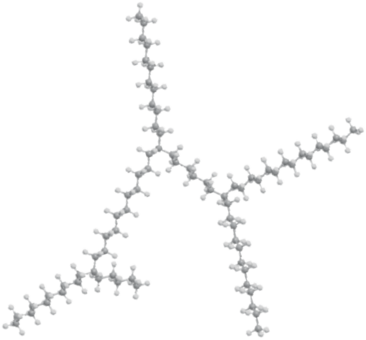
- The first method of classifying polymers is based on the chemistry that creates them, and the simplest chemistry one can use clicks monomers together without any by-products forming. This kind of polymer is called an addition polymer.

- Addition polymers are generally created from monomers, which come together in a process called chain growth. The individual monomers aren't particularly reacted, but in the presence of a special chemical initiator, each time a new monomer connects, the monomer becomes reactive, thereby causing the chain to extend.

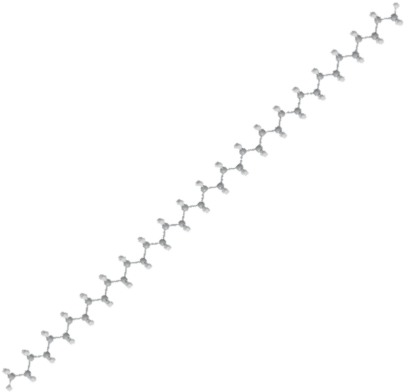
- An example of this is polyethylene, in which we use an organic radical as an initiator to kick off the reaction between and among various numbers of ethylene molecules. As the reaction takes place, it grows from one end of the chain to the other, and in doing so, we can create long hydrocarbon chains of hundreds, and even thousands upon thousands, of these individual monomer units before the activated radical is finally quenched in reaction with another radical somewhere in the mixture.

- Using this process, we can create hydrocarbon molecules of tremendous size and complexity. For example, we can create long chains of hydrocarbons called high-density polyethylene that are used in the manufacturing of toys. Or we can introduce more branching into the molecule, creating low-density polyethylene, which is used in the plastic bags you find in your local grocery store.

LOW-DENSITY POLYETHYLENE (LDPE)



HIGH-DENSITY POLYETHYLENE (HDPE)



- All of these materials are made from one very simple starting material: ethylene gas. Just a little bit of careful consideration in how we put together the polymer can create a drastically different and useful material.

- Because this reaction takes place with no by-products generated, its product is classified as an addition polymer.

- Polyethylene is a remarkable product, considering how simple its structure is. Since its discovery in 1933, scientists have developed ways to control the size and even the branching of this structure to create a variety of polyethylene materials.

- But ethylene isn't the only monomer that works in this strategy. Its 4 hydrogen atoms are just placeholders. Replacing them with different atoms, or groups of atoms, creates even more useful materials, such as polyvinyl chloride, commonly known as PVC, or polystyrene, which is constructed from styrene monomers and used in everything from seat cushions to CD jewel cases.

SYNTHETIC POLYMERS: CONDENSATION POLYMERS

- The second class of polymers is condensation polymers, which differ from addition polymers because they produce a by-product when monomers come together to form a chain. These by-products are usually very small and often include water, from which the process gets its name, even though production of water is not a requirement for a polymer to fit into this class.

- Condensation polymers differ from addition polymers in the sense that they rarely need an activator to initiate the polymerization reaction. This makes them fairly easy to create in some instances, but it makes them more difficult to control.

- If we have a collection of monomers, all of which can react with one another, we go through a process called step growth instead of chain growth. It's not as controlled of a process; the resulting molecules are often of drastically different sizes.

- Although they're more difficult to control, they're very often used because they can produce some remarkably useful and versatile materials. For example, consider nylon 6,6, in which we take 2 different types of monomers—in this case, a molecule known as adipic acid and one called hexamethylenediamine—and they react with one another in a step-growth process that produces water as a by-product. The water energetically drives the reaction forward, leading to relatively large molecules joined by special bonds called amide bonds.

- Condensation polymers include not only nylon, but other familiar polymers as well, such as the polyester material Dacron, the Kevlar in bulletproof vests, and the polycarbonate material Lexan, which is used to make bulletproof glass.

HOMOPOLYMERS AND COPOLYMERS

- A second method of characterizing polymers is based not on the type of bond that holds them together, but rather on how many different monomers are used and how they are arranged.

- Polyethylene consists of only ethylene monomers strung together into a long chain—that is, just one kind of monomer making up the entirety of the polymer. But nylon 6,6 is a polymer that is made by condensing 2 different monomers together in the chain.

- When 2 or more monomers are included in the same macromolecule, the resulting polymer is called a copolymer. Copolymers are amazing because they open up a whole new dimension in polymer design. It is no longer just about how long or branched a polymer is, but how the multiple monomers are arranged.

- Regardless of how they're synthesized, we can classify polymers also based on how they're put together at the monomer level. For example, consider a molecule that has 2 different types of monomers. If we put these monomers together in an alternating pattern, we get an alternating copolymer. Nylon 6,6 is an example of an alternating copolymer.

- Another type of copolymer is a random copolymer, in which we still have 2 distinct monomers, but those 2 distinct monomers can react with not only monomers of a different type, but also monomers of the same type. When this happens, we get a random orientation of them within that polymer. This is a classic example of how we can create heat-sensitive or heat-resistant shrink-wraps that are used on food.

- A third type of copolymer is a block copolymer. With this type of copolymer, we have large stretches of one monomer followed by large stretches of the other monomer within the same large macromolecule. Block copolymers are a great way to create things like industrial-strength adhesives and also some very specialized rubbers that are often found in modern tire formulations.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 494–501.
Cobb and Goldwhite, *Creations of Fire*, pp. 337–346.
Masterton and Hurley, *Chemistry*, 23.1–23.2.

QUESTIONS

1. Consider the geometry of polyethylene macromolecules. Why are less-branched polyethylene polymers called high-density polyethylenes while branched polymers of the same type are called low-density polyethylenes?

2. Some polymers, such as polyethylene, are so chemically tough that they cannot be broken down in natural systems (i.e., biodegraded) and instead must be recycled. What structural or compositional differences might make other polymers more biodegradable?

Biological Polymers

LECTURE 51

Polymers are everywhere in living systems, and 3 billion years of evolution has led to some truly remarkable polymer chemistry. In this lecture, you will learn about biopolymers—polymers that are used in living systems. Biopolymers are not terribly different from synthetic and semisynthetic polymers: They are constructed from monomers, are often formed using condensation reactions, and exist some as homopolymers and some as copolymers. But aside from having biological functions, what makes biopolymers unique and fascinating is their complexity. Living systems exercise control over synthesis of these polymers that no chemist could ever hope to achieve in a beaker.

CLASSES OF BIOPOLYMERS

- There are 3 broad classes of biopolymers: polysaccharides, polynucleotides, and polyamides.

- Polysaccharides are built from sugar monomers. Cellulose is a biological polymer.

- Polynucleotides are formed using molecules known as nucleic acids. The classic examples of these are DNA and RNA. These polymers drive the storage and transmission of our genetic code.

- Biological polyamides use the same linkage that holds nylon polymers together, but their complexity gives them vast functionality, from the collagen in your skin to the hemoglobin carrying oxygen through your body.

POLYSACCHARIDES

- Chemists refer to sugars as saccharides. One of the simplest saccharides is glucose. One molecule of glucose can pair with another simple saccharide, fructose, to produce the compound that most people know as table sugar, or sucrose.

- Sucrose is formed when a condensation reaction links these 2 units together in a very specific arrangement, creating a new compound with chemical properties that are slightly different than either of the individual components.

- This is also true of the sugar maltose, which forms when 2 glucose molecules come together to form what is called a dimer—a molecule consisting of 2 linked units. These relatively small molecules can be very quickly broken down into glucose, which is burned for energy in your cells.

- When there is excess glucose available, the body stores it. In your body, the storage system that your cells use to keep plenty of glucose on hand is a polymer. But the polymer that your body makes out of glucose is not the same as the cellulose from plant cell walls. Cellulose is too strong, and humans lack the ability to break it down to recover the glucose inside.

- Instead, we use the polymer glycogen, which uses glucose monomers linked together in a different geometric arrangement than cellulose. The long, slender fibers of cellulose are replaced with a highly branched system of connected monomers.

- This different geometry changes the properties of the polymer, making it less fibrous and easier to break down chemically for quick energy usage.

- But the versatility of polysaccharides doesn't end there. In fact, nature has created some semisynthetic polymers—molecules like the chitin that makes up the armor of arthropods like crabs and insects. The molecule chitin is actually a polysaccharide containing a chemically modified glucose molecule called N-acetylglucosamine.

- The new functional group changes the way that individual strands of chitin interact with one another, and what was once fibrous cellulose is now a sheet of chitin armor. When combined with calcium carbonate salts—as it is in crabs, for example—chitin armor is so rigid and tough that crabs must periodically evacuate their old shells so that they can grow.

POLYNUCLEOTIDES

- As a structural material and for energy storage, polysaccharides are top notch, but they typically consist of just one or 2 types of sugar monomers, limiting the variability of their composition. Two people's glycogen are exactly the same.

- But the body has another polymer at its disposal—one with tremendous variability. It has so many possible combinations of monomers that every living thing on Earth has a different version of it—unless, of course, you are an identical twin.

- Deoxyribonucleic acid (DNA) is a biopolymer that is so large and complex that it can store within it all the information needed to make you who you are.

- The story of DNA begins in 1869, when Johann Friedrich Miescher extracted this substance from the nuclei of cells that he was studying. Miescher dubbed this material "nuclein"—an indication of its origins.

- A Russian researcher named Phoebus Levene started scientists on the long road to understanding the structure of this critical material. He was able to break the so-called nuclein down into its constituent parts. He found phosphates, 4 organic bases—adenine, thymine, cytosine, and guanine—and, interestingly, a sugar called ribose.

- In 1940, nearly 70 years after Miescher's discovery, Erwin Chargaff noticed that when he isolated all 4 of the bases, cytosine and guanine were always present in equal amounts, and so were adenine and thymine. It was an intriguing observation—one that hinted at the structure of DNA. As tantalizing as this observation was, debate still raged about exactly what DNA was and how the molecule was put together.

› The world would have to wait another decade to settle the argument. The key piece of data that unlocked the secrets of this biopolymer was one from the same technique that had proven Hermann Staudinger right about cellulose: X-ray crystallography.

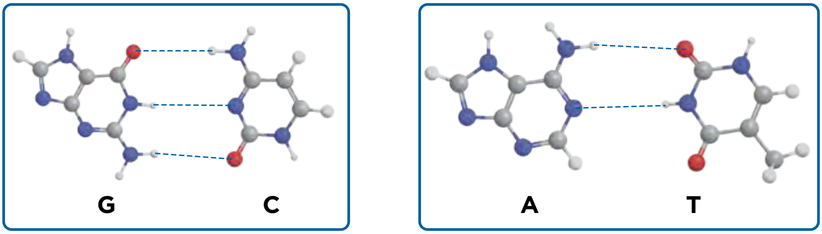
› The lab of Maurice Wilkins and Rosalind Franklin, as well as that of James Watson and Francis Crick, generated that X-ray crystallography data almost concurrently. A race to press ensued, and Watson and Crick prevailed, securing their place in history as the widely credited discoverers of the DNA double helix.

› Watson and Crick's structure revealed not only the elegant twist in this polymer of life, but also its inner workings. Everything that was already known to be a part of DNA was there. Ribose-like units were held together by phosphoester bonds, and attached to those ribose-like units were the 4 base pairs: adenine, cytosine, guanine, and thymine.

› The structure demonstrated why Chargaff had noticed the equal proportions of cytosine and guanine, as well as those of adenine and thymine. The solved structure of DNA showed 2 strands with complementary pairs of bases that came together almost like the teeth of a zipper.

› Watson-Crick base pairing drives the formation of DNA. A network of 2 hydrogen bonds holds adenine (A) and thymine (T) together in such a way that the double helix of DNA can form and be held together tightly. Similarly, a network of 3 hydrogen bonds form between guanine (G) and cytosine (C), and that holds the DNA together even more tightly. That hydrogen-bonding network that holds the DNA together simply isn't there when we try to pair G with T or A with C.

WATSON-CRICK BASE PAIRS



- As elegant and remarkable as these features of DNA are, what really makes this molecule of life useful is the fact that it is a polymer. DNA strands can reach truly staggering lengths in higher organisms.

- The human genome consists of about 5 billion base pairs strung together. That is enough DNA to create a 1.8-meter strand when extended completely. This makes DNA the undisputed king of information storage. Five billion letters go into the code that defines who you are, at least in a biochemical sense.

- But DNA isn't the only polynucleotide that your body relies on. DNA is the vessel for genetic codes. It is the template—the ultimate source of information. So like any archive, it is designed to last you your entire life.

- But the genes in your DNA are merely instructions. Those instructions have to be carried out. And the task of turning the information in your DNA into you falls to a very close chemical cousin: ribonucleic acid (RNA). RNA is remarkably similar to DNA, but with 2 very special differences. The ribose sugar is not missing the hydroxyl group like DNA is, and it uses the base uracil rather than thymine. Both of these changes make RNA less stable.

- RNA serves as a messenger. It is designed to carry information from your DNA to a sophisticated molecular machine called a ribosome, where it is used to create proteins and enzyme that you need to survive.

- Once a message is delivered, your body recycles RNA, which can be broken back down into its constituent pieces and reconstructed in a new order to carry a new message. So, RNA doesn't need to last your entire life. Indeed, it is actually designed to be easier to disassemble than DNA. This way, it can be rebuilt to carry the message from a new gene and continue to drive your biochemistry.

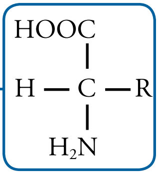
POLYAMIDES

- Polyamides—also known by their biologically relevant name as proteins—were discovered fairly early in the development of our understanding of biochemistry. Many natural sources of fairly pure proteins are available from biological sources, such as the whites of eggs. Even in the earliest days of protein experimentation, it was noted that they had a certain nutritional value that other foodstuffs could not replace.

- For this reason, Swedish chemist Jöns Jacob Berzelius suggested that they be named protein, from the Greek term for "first" or "in the lead." The name stuck, and the rest is history.

- Proteins are the body's handymen. While DNA stores information and RNA translates and transfers information, it is proteins that make up the materials in your muscles, carry oxygen to your cells for respiration, and moderate just about every chemical reaction that goes on inside your body.

- Proteins are polymers that are made from monomers called amino acids. Amino acids have 2 functional groups: an amine and an acid, both of which are critical to how amino acids function in biological systems. Each amino acid is identifiable by its unique side chain, which is designated as R in the following.



$$\begin{array}{c} \text{HOOC} \\ | \\ \text{H}-\text{C}-\text{R} \\ | \\ \text{H}_2\text{N} \end{array}$$

- Amino acids come together chemically to create the large biopolymers that we rely on every day through a condensation reaction much like synthetic polymers go through. When 2 amino acids come together to begin forming a protein—or a peptide, as we might call it when it's very short—a condensation reaction takes place. During that condensation reaction, water is formed. In addition to water, there is a functionality called an amide bond.

- Our bodies use 20 amino acids. But why 20? DNA does just fine with only 4 monomers. The reason is that many proteins are much smaller polymers than an entire strand of DNA. Having a larger library of characters increases the potential variability of smaller biopolymers like proteins.

- The second reason is that proteins tend to take on some remarkably complex shapes. Far from just a double helix like DNA, protein backbones can take on helical shapes, extended strands, and even turns that cause them to ball up on themselves in very specific ways. Often, the complex structures they form are dictated by the interaction of side chains with one another.

- At least in part, it is the fold of a protein that gives it its function. Properly folded proteins are powerful biological catalysts needed to mediate your biochemistry. Because they are so essential, improperly folded proteins can lead to debilitating illness, such as Alzheimer's disease and sickle-cell anemia.

- Proteins generally serve one of 2 roles in the body: as structural materials (like our skin, hair, and fingernails) and as catalysts for chemical reactions in our bodies that keep us going. These kinds of proteins are called enzymes, and they are the worker bees of your cellular machinery, speeding up and slowing down such critical processes as oxygen transport and nutrient metabolism, as well as repairing DNA.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 1093–1107.
Cobb and Goldwhite, *Creations of Fire*, pp. 349–358.
Masterton and Hurley, *Chemistry*, 23.3–23.4.
Watson, *DNA*.

QUESTIONS

1 Proteins serve many functions in many regions of living cells. Some are anchored in the low-polarity cell membrane and others are dissolved into the water-rich cytoplasm of the cell. Which amino acid residues do you expect to find most often in proteins that dissolve easily into the water-rich cytoplasm of a cell, and why?

2 Chemists have devised ways to prepare and isolate biopolymers in the laboratory both for study and to create useful products. What are some products that make use of biopolymers as ingredients?

Medicinal Chemistry

LECTURE 52

In this lecture, you will explore drug chemistry. You will learn about how many enzymes work, catalyzing reactions by what is known as the lock-and-key mechanism, and you will also learn about the phenomenon known as enzyme inhibition. From simple, over-the-counter anti-inflammatories to antibiotics to anticancer drugs, you will discover just how remarkable it is that many small molecules have the capacity to fine-tune or disrupt our most basic biological chemistry.

THE LOCK-AND-KEY MECHANISM

- Our understanding of how enzymes function finds its beginnings just over a century ago, when Emil Fischer proposed that enzymes and the molecules that they help to modify might work by what he called a lock-and-key mechanism.

- In this theory, a small molecule to be modified, called a substrate, must dock with an enzyme at a very specific location on that enzyme, known as the active site, to induce it to react. The fold of a protein presents a surface of various polar bonds and functional groups in a very specific arrangement, and at that one very specific location, all of the atoms are arranged to perfectly interact with the substrate molecule.

- This very specific set of interactions ensures that only the proper substrate will dock with the active site, giving enzymes their amazing ability to carry out specific reactions very rapidly.

- Once the substrate has been modified, it no longer fits perfectly into the active site and is released from the enzyme, which is now ready for another round.

- The lock-and-key model has proven to be remarkably versatile, describing the action of a number of enzymes in processes as varied and important as pain transmission, oxygen transport, removal of toxins from the bloodstream, and many more.

- Cyclooxygenase (COX) enzymes help convert a fatty acid called arachidonic acid into a prostaglandin, a class of compounds that trigger inflammation in infected or injured tissues. In this case, arachidonic acid is the substrate and is bound to the COX enzyme active site, where oxygen is added to the molecular structure.

- Once the new bond motif has been added, the product molecule is not held as tightly to the active site, and it is released, making the active site available for another molecule to dock. The arachidonic acid is on its way to becoming a prostaglandin, able to trigger inflammation in muscles and joints.

- In the case of injury, inflammation is essentially blood rushing into the area to help carry nutrients in and toxins out. It is beneficial to an extent. But when the inflammation gets to be too much for your own good, decreasing joint mobility and causing pain, there is a way to shut this process down and get some relief.

ENZYME INHIBITORS

- In the lock-and-key schematic, the substrate, or key, must fit into the active site, which can be thought of as a keyhole in the lock of the enzyme, to function. If you wanted to stop someone from opening a lock to which that person has the key, you might try to disable the lock by blocking the keyhole—and this is exactly what many small-molecule drug compounds do.

- They imitate the substrate, docking with the enzyme's active site, but never reacting. This means that a small number of these molecules can shut down enzyme activity in just as selective a way as the enzymes can carry out reactions.

- This phenomenon is known as enzyme inhibition, and although not all drug molecules act in this way, a striking number of them do. Inhibition can occur by a number of mechanisms as well, but the case in which the drug molecule competes directly for the active site is called competitive inhibition.

- When it comes to competitive inhibition, we are looking for the drug molecule that best sticks to the active site of the enzyme, which we can model as an equilibrium process.

- Small molecules that bind to enzymes are called ligands. Let's think about the equilibrium between the binding of a ligand to an enzyme and its removal from the enzyme.

- The following is an equilibrium in which we use generic symbols to indicate these players: E for the enzyme and L for the ligands. The equilibrium product is the enzyme and ligand bound together while they're interacting with one another through non-covalent, intermolecular forces.

$$E + L \rightleftharpoons EL$$

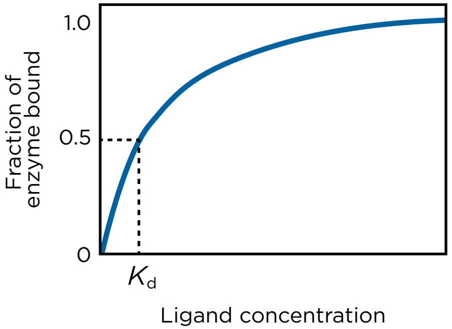
$$K_{eq} = \frac{[EL]}{[E][L]}$$

- If we model this process as an equilibrium, we can assign it an equilibrium constant for any given ligand and enzyme system, K_{eq}, which for this process is the enzyme bound to the ligand concentration divided by the separate enzyme and ligand concentrations within the system.

- When we do this in the direction in which the reaction is written—so that we're observing the binding of ligands to the enzyme, where the product is the bound ligand—we can call this K_a, or the association constant. These numbers tend to be very large for very effective ligands—so large, in fact, that biochemists prefer to think of these in terms of the reverse reaction.

- When we flip the equilibrium over—making the enzyme and ligand bound together as the starting material and the free ligand and enzyme as the products—we have to remember that because we've switched their identity in the reaction, we also have to switch their location in the equilibrium constant expression. To convey that we've done this, we change K_a, the association constant, to K_d, the dissociation constant.

$$K_d = \frac{[EL]}{[E][L]}$$



- In this case, we have concentration times concentration divided by concentration, which means that if we assigned units to the values within the expression, we will always get a number in terms of concentration. The smaller K_d is, the stronger the ligand binds.

- Chemists who want to survey how strongly a ligand binds to a particular enzyme need a technique that will allow them to get this K_d equilibrium constant.

- Fortunately, most enzymes work in solution the same way that they do inside your body. If we want to measure how well a ligand sticks to an enzyme, all we have to do is create a solution of that enzyme and progressively add more and more ligands to the system and measure the effects—specifically, how much enzyme is bound as a function of the ligand concentration.

- When we do this for simple processes, we get a curve, with the fraction of bound enzyme on the *y*-axis and the ligand concentration on the *x*-axis. The midpoint of that curve, where the fraction of bound ligand is exactly 0.5, is also equal to K_d.

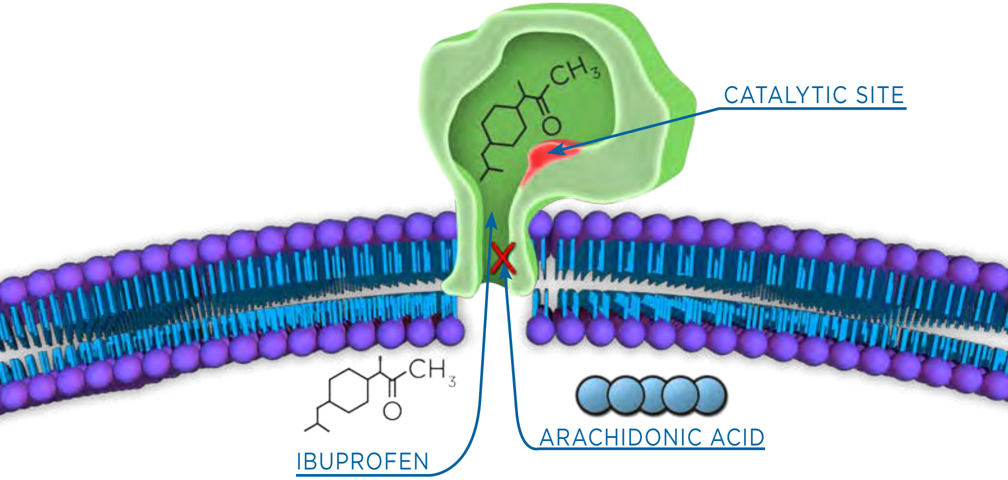
- By creating a solution of the enzyme we'd like to inhibit and then progressively adding more and more of the new drug candidate, we can determine exactly what K_d is for that candidate. Then, we simply take all the potential ligands that we'd like to consider as medicines and line them up in order of how tightly they bind to the enzyme. The smaller K_d is, the greater the potential therapeutic use of the particular compound would be.

- Researchers prospecting for a new pharmaceutical product that works by this mechanism can simplify their search for molecules that have very low K_d values with specific enzymes associated with the process that they are trying to shut down.

ANTI-INFLAMMATORIES

- Ibuprofen is one of a class of compounds known an NSAIDs, or nonsteroidal anti-inflammatory drugs. If we consider again the COX enzyme, but this time in the presence of ibuprofen, ibuprofen makes its way into the active site that was meant for arachidonic acid. It clogs up the active site of the enzyme and renders it less effective through competitive inhibition.

- Not only can ibuprofen get into the active site, but it can also get out again. The association of ibuprofen with the COX enzyme is an equilibrium process, and chemists can model this process using the simple rules of equilibrium. So, chemists can many times screen test candidates for new drugs by measuring just this sort of equilibrium in a laboratory—long before a potential drug is ever tested on a living soul.



ANTIBIOTICS

- Bacteria are often harmless to us, and sometimes even beneficial, but sometimes bacteria can take a sinister turn, invading our bodies, stealing nutrients that we need, upsetting our biochemical balance, or even consuming our own flesh.

- Bacterial infections have been a fact of life for as long as complex organisms have existed. Our higher-order bodies offer a safe, nutrient-rich environment for pathogenic bacteria to thrive.

- In the modern, developed world, we have the luxury of not worrying much about the risk of death or serious injury from bacterial infections because of a class of drugs called antibiotics, possibly the most influential class of drug compound ever created.

- Penicillin is just one example of an antibiotic. Penicillins have a beta-lactam ring that is strained and that opens and covalently bonds to an enzyme called transpeptidase, which is used by certain types of bacteria to create a feature in their cell walls that people don't have.

- The deactivation of the transpeptidase enzyme inhibits the ability of certain bacteria to create and repair cell walls. What is truly remarkable about penicillin is that it not only docks with the active site of transpeptidase, but it also reacts with it to form a covalent attachment.

- This special form of competitive inhibition is called suicide inhibition, because the drug sacrifices itself in an irreversible covalent bonding to one enzyme molecule. This effectively makes K_d equal to 0.

- With their transpeptidase enzymes permanently shut down and their cell walls weakened, the bacteria break open, resulting in their death.

ANTICANCER DRUGS

- When cancer strikes, your own cells go haywire, growing and dividing rapidly—and sometimes even spreading throughout the body. Cancer cells are runaway cells that can no longer moderate their own growth. They uncontrollably grow and divide.

- Your cells mutate constantly. Your body is remarkably good at reliably copying the DNA needed for one cell to become 2, each with a perfect copy of the genome of the parent cell. But more than 2 trillion perfect copies in a day is too much even for the miracle of nature that is your body. Sometimes, the new cells are failures.

- The good news is that these failed copies have a failsafe: a type of programmed cell death called apoptosis. Apoptosis plays several roles in cell division and growth, but it is this idea that it acts as a failsafe in damaged cells, causing them to destroy themselves rather than make new copies of the damaged cells, that is probably the only reason that any of us have lived as long as we have.

- But what happens when a mutation or cellular damage actually damages the genes needed for the apoptosis process to take place? You have wildly developing cells that have no way of sacrificing themselves. You have cancer.

- One method that researchers try to treat tumors is with drugs designed not to shut down the process, but instead to reactivate the apoptosis pathway, in the form of chemically assisted cellular suicide.

READING

Salyers and Whitt, *Revenge of the Microbes*, chaps. 1–5.
UC Davis ChemWiki, “Pharmaceuticals.”
http://chemwiki.ucdavis.edu/Core/Biological_Chemistry/Pharmaceuticals.

QUESTIONS

1 Organisms are constantly evolving and producing new enzymes to cope with stresses. If a bacterium is stressed by the presence of an antibiotic compound, how might that bacterium use proteins of its own to resist that antibiotic?

2 How might a drug’s ability to bind strongly to more than one kind of enzyme help explain the phenomenon of drug side effects?

Poisons, Toxins, and Venoms

LECTURE 53

In this lecture, you will learn about poisons, toxins, and venoms—all of which are chemical compounds that are naturally occurring and potentially deadly. Poisons can be thought of as any chemical that disrupts the normal biological functions of a living system. Toxins, a subclass of poisons, disrupt biological systems but are created by another biological system. A venom is a toxin that one animal transfers to another by injection, either as a predatory or defensive tactic.

POISONS

- Poisons are substances that have negative health effects when we are exposed to them in concentrations or amounts commonly encountered. Poisons have played a profound role in the progress of human history, perhaps most famously as a tool of assassins throughout the histories of the Greek, Roman, and Byzantine empires.

- Poisons continue to influence our behavior as a species today. Although the rather nefarious practice of political assassination is far less common in the modern world, it does still happen from time to time. Bulgarian writer and political dissident Georgi Markov was felled in 1978 by a small pellet of ricin that was craftily injected beneath his skin by a mysterious, umbrella-carrying man in London.

- Most people are familiar– with classic poisons like arsenic, cyanide, and thallium, which are inorganic, nonbiological materials that are so acutely toxic that only a small amount of them is needed to bring about disastrous health effects.

- As interesting as other poisons might be, the granddaddy of them all is arsenic. There is evidence that in the 1st century A.D., arsenic in its sulfide form had been discovered and used by Greek physicians to aid in tooth extraction.

- But it was quickly recognized that ingestion of large quantities of arsenic-containing compounds had catastrophic effects on human health, leading to violent abdominal cramping, vomiting, and often death from shock.

- In the 16th century, a Swiss physician named Paracelsus, the first recognized toxicologist in human history, published the first detailed instructions for the production of metallic arsenic from its naturally occurring sulfides, launching it to the forefront of poison technology. Thanks to his work, arsenic quickly became the poison of choice for anyone with the resources to get it and settle a score.

- The potency of poisons is measured using a system similar to the ED50 designation in drugs. But instead of an ED50, which is the effective dose for 50% of a population, poisons are characterized by their LD50—the lethal dose for 50% of a population. Arsenic's LD50 of about 15 milligrams per kilogram in rats translates to about a 1-gram dose—an amount of arsenic about the size of a jellybean—being potentially fatal for humans.

- Arsenic remained the poison of choice in Western society for many centuries. As recently as the Renaissance, this colorless, odorless, tasteless material was used so frequently that it gained the nickname "inheritance powder."

- How does arsenic do its damage? What is it about this element that makes it so dangerous when consumed? The answer lies just above it in its elemental group on the periodic table, where we find phosphorus, an element that often appears in biochemistry as phosphate. Phosphates serve multiple critical roles in biology, including holding your DNA together, as well as playing roles in storage and use of energy.

- It is that last function that makes humans vulnerable to arsenic. Adenosine triphosphate (ATP), a compound that helps your body manage energy storage, is an adenosine base with 3 phosphate groups condensed to it in a chain. Removal of a phosphate group creates adenosine diphosphate (ADP) and a considerable amount of chemical energy that your body taps to keep itself going.

- Because arsenic has a $4s^2\ 4p^3$ electron configuration, the complex ion arsenate is a very similar ion to phosphate—so similar that it can replace phosphate in ATP molecules, causing a malfunction in the energy storage and transmission process in your body.

TOXINS

- Toxins are a type of poison—one that is generated biologically. In the nearly 3 billion years since life formed on this planet, a battle has ensued that pits living things against each other in the struggle for existence. Certain plants and animals have been able to hedge their evolutionary bets by creating substances that make them less attractive as a food source for others, or even that go on offense, beating back competing life-forms to increase the chances that they will have enough resources to survive.

- A classic example of toxins are those compounds created by plants like hemlock. Hemlock plant produces copious amounts of the molecule coniine, which acts like many drugs, binding to proteins in your body that need to function properly to keep you alive.

- It impersonates nicotine, another toxic substance that is found in tobacco plants. Both of these molecules bind to receptors that process ions in your body. Usually, the cause of death is respiratory paralysis, as the muscles that flex to fill and empty the lungs fall still.

- Nicotine is produced by tobacco plants to discourage insects from eating them. It is a natural defense mechanism for the plant. We tend to think of nicotine as a relatively weak toxin compared to others, but in fact, the injection of just a small amount—not much more than you would find in a cigar—can be fatal.

- Plants aren't the only members of the biosphere that have adopted this kind of chemical survival strategy. Animals have their share of potent toxins, too. In fact, the deadliest toxin that has been isolated—batrachotoxin—came from the back of the poison dart frog.

- Excreted by glands of the poison dart frog, this compound acts by binding to proteins that transport sodium ions across cell membranes as part of normal muscle contraction. This mechanism of action is quite common among toxins and poisons, but what makes batrachotoxin so special is its potency.

- This molecule binds so powerfully to sodium-ion-channel proteins that the LD50 is estimated to be 2 micrograms per kilogram, meaning that a human could be killed by much less than 1 milligram of the toxin—a mass one-thousandth the size of a pea.

- Because the toxins produced by these plants and animals are relatively simple small molecules, they tend to be capable of surviving a trip through the gastrointestinal tract, making them truly poisonous. All a predator has to do it take a taste of one of these little creatures and its life is in jeopardy.

VENOM

- Just one sting from a scorpion or box jellyfish or one bite from a copperhead snake can take the life of an animal hundreds of times its size. Many of nature's predators have developed systems to make their bite or sting as lethal as possible—not by the direct damage done by the bite or sting, but by potent chemicals introduced at the site of the bite wound.

- It is quite remarkable that animals like these can produce and carry around a venom so toxic that it can kill, yet they are unharmed. The venom kills prey, which the predator now eats, and the predator is just fine. Venoms from predatory animals are not only very potent, but they are also much more complex at the molecular level than most poisons are.

- Venoms are proteins. They are made of the same amino acids as the rest of the proteins in our bodies. Once their job is done and the predator starts to chow down, the predator's digestive tract treats the venom like any other protein, breaking it down into amino acids for nutrition, rendering it nonlethal.

- But before all that happens, the venom is injected into the prey, bypassing the digestive tract altogether and surviving the transfer intact to paralyze the muscles of prey, in some cases leaving it defenseless to further attack and in other cases to kill it outright by stopping its heart or lungs from functioning.

- But how does the venom accomplish this? To answer that question, we first have to consider some of the chemistry behind muscle contraction. When your muscles flex, the cells making up the muscles are responding to the flow of certain ions across their cell membranes.

- But that raises an issue. Cell membranes are made primarily of molecules called phospholipids, which come together to form a very low-polarity barrier that holds the contents of the cell inside.

- How do you get a charged potassium ion, for example, to cross that barrier? On the outside of the cell, the ion is happy, solvated, and stable, interacting well with the dipoles of the water molecules around it in a favorable ion-dipole interaction.

- But for muscles to function properly, that potassium has to cross the membrane, sacrificing all of that stabilizing interaction with solvent only to be surrounded by long hydrocarbon tails that do not have any polar bond to speak of.

- It is an environment that potassium simply isn't going to become a part of—not even for a split second as it moves into the cell. But cells have developed a clever way to solve the problem. Cells use special proteins called ion channels.

- Some amino acids have very low-polarity side chains, and others have very high polarity groups. When inserted into a cell membrane, a folded ion-channel protein presents a very low-polarity face to the hydrocarbon tail of the phospholipids, allowing it to embed itself into the cell membrane. At the top and bottom are higher-polarity side chains that are interacting with the water on either side of the cell membrane.

- Most importantly, the interior of the channel itself is loaded with polar bonds waiting to interact with potassium ions favorably as it makes its trip across the membrane. When in place, this magnificent structure can transport potassium ions across the cell membrane to help keep your muscles working correctly. But the powerful short proteins, or peptides, in venom shut down these remarkable creations with deadly efficiency.

- Most animal venoms are protein-based. Because they are meant to be injected into the victim's bloodstream by a bite or sting, this chemical strategy works. The venom bypasses the digestive system and goes straight to work, paralyzing victims by blocking the flow of ions across cell walls.

- As bad a reputation as venoms have, they also have incredible potential for positive applications. In particular, these molecular assassins are so potent and lethal to human cells that researchers want to find ways to harness that lethally to kill cancer.

READING

Parascandola, *King of Poisons.*

UC Davis ChemWiki, "Case Study: Elemental Toxicity in Animals."
http://chemwiki.ucdavis.edu/Core/Inorganic_Chemistry/Case_Studies/Case_Study%3A_Elemental_Toxicity_in_Animals.

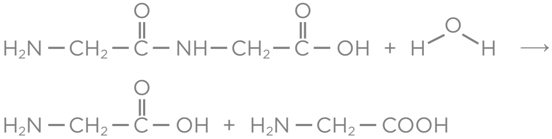
QUESTIONS

1 Antivenoms, such as those used to treat snakebites, are themselves proteins. How might these proteins render a venom ineffective?

2 Many venoms are polyamides, which are biological polymers. These polyamides undergo hydrolysis when ingested, making them ineffective unless injected. Draw a balanced chemical reaction for the hydrolysis of an amide bond in a diglycine peptide.

Answer

2) Note that there are many ways to represent molecules in chemical reactions. The following example uses structural formulas for the molecules.



$$\mathrm{H_2N-CH_2-\overset{\overset{O}{\|}}{C}-NH-CH_2-\overset{\overset{O}{\|}}{C}-OH + H{-}O{-}H} \longrightarrow$$

$$\mathrm{H_2N-CH_2-\overset{\overset{O}{\|}}{C}-OH + H_2N-CH_2-COOH}$$

Chemical Weapons

LECTURE 54

In this lecture, you will explore a dark side of human pursuit of the science of chemistry as you investigate man-made chemicals as weapons of war. As you will learn, in just a few decades and over the course of 2 global conflicts, human chemists have quickly closed the gap on nature when it comes to using chemicals for combat—not one of our proudest achievements.

CHLORINE GAS

- Late in the afternoon on April 22, 1915, German and French military lines were facing off along a long front that ran through Belgium. The standoff had lasted for months. Miles and miles of trench had been dug to protect the ground troops tasked with holding back the advance of Kaiser Wilhelm's war machine.

- Near the hour of 5 pm, a 4-mile-wide cloud of yellowish-gray gas began drifting across the battlefield near the city of Ypres and into the French trenches. Men fled on foot and on horse, abandoning their weapons and equipment as they ran from the advancing cloud. A gap miles wide opened up in the French lines, exposing a tremendous opportunity for Germany to advance and take ground.

- On that day in 1915, the most infamous chemical attack in history took place at the hands of a man named Fritz Haber, one of the most famous and infamous personalities in the history of chemistry, if not of all humanity.

- Haber and the world knew well the dangers of chemical warfare. In fact, those dangers were so well understood that the developed nations of Europe signed a pact in 1899 forbidding the use of chemical weapons on the battlefield.

- But in the spring of 1915, World War I had ground to a stalemate, and Germany was looking for a way to get their western front mobilized again and keep marching toward (and if they had their way, right through) France. Desperate times will make people do desperate things.

- Having already determined how to create large quantities of fixed nitrogen for the German war effort using his famous Haber-Bosch process, Haber received a special appointment to head up a German chemical weapons program. This time, his job would be devising ways to use his chemical genius on the battlefield.

- His first attempt took place in 1915, when Haber ordered the release of chlorine gas from an array of more than 5000 tanks that had been buried near the French line under the cover of darkness in the preceding months.

- Chlorine gas is a diatomic halogen. Its lack of a dipole makes it a gas in spite of the relatively high molecular mass of about 70 atomic mass units. Its dispersion forces aren't enough to make it a liquid, but the relatively high molecular mass ensures that this gas is denser than air. Chlorine gas can also be stored in tanks and released.

- When released, a cloud of chlorine gas will ride along the ground, carried by the wind. This gives it the ability to move and settle into trenches and fortifications, where it can do the most damage.

- When chlorine gas reaches its target, the chemical properties of chlorine come into play. Chlorine gas has a relatively low bond enthalpy, making it fairly reactive and allowing it to undergo a number of potentially dangerous reactions when inhaled—none more dangerous, potentially, than the reaction of chlorine gas with the moisture inside your lungs.

- When chlorine gas reacts with liquid in your lungs or water in your lungs specifically, you get 2 different kinds of by-products from that reaction: hypochlorous acid, which is a fairly weak acid, and hydrochloric acid, which is a strong acid. Chlorine creates acid inside the lungs. If the chlorine gas stays in the lungs long enough, it can be extremely dangerous.

- Haber's seemingly inefficient delivery method—planting 5000 tanks of chlorine gas in the ground under the cover of darkness—was used as a sort of work-around to the chemical weapons ban agreed to in The Hague pact of 1899. Germany insisted that the pact only banned ordinance-based chemical weapons. Because Germany wasn't launching shells, it claimed, it wasn't violating the pact.

PHOSGENE

- Not to be outdone by their German counterparts, the allies of World War I launched their own chemical weapons programs in response to the attacks at Ypres. As both nations advanced their efforts in this vein, a newer, more effective weapon came into use.

- The next generation of chemical weapon is called phosgene gas. Like its predecessors, phosgene is denser than air, easily inhaled, and reacts with moisture in the lungs to create hydrochloric acid. It is slightly denser than chlorine gas and deadly at ⅒ the dose.

- Not only does the reaction of phosgene with moisture create more moles of potentially deadly hydrochloric acid, but it also does so spontaneously. Phosgene's potent reactivity makes it more effective than chlorine.

- Unlike chlorine, which produces a characteristic odor, warning victims that it is in the air, phosgene is essentially odorless, so even at dangerous concentrations, it can be difficult to detect. Furthermore, phosgene does not mix well with water like chlorine gas does, so the reaction that breaks it down into the large quantities of lethal hydrochloric acid is slower—so slow, in fact, that a lethal dose can be inhaled long before any ill effects are felt.

- This made phosgene gas the poison of choice throughout most of World War I. Phosgene is so deceptively odorless and painless to inhale that many men lost their lives after failing to use gas masks in response to attacks that they never even realized had happened.

- It is estimated that about 85% of the deaths by chemical agents in World War I can be attributed to phosgene gas fired from artillery shells as both sides began to flagrantly abandon The Hague pact in their desperate search for victory.

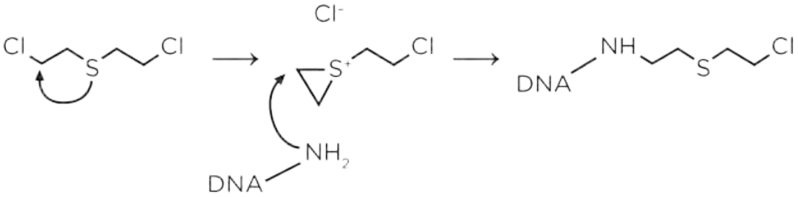
MUSTARD GAS

- The final development in chemical warfare during World War I came late in the conflict. In the summer of 1917, German shells rained down on British positions containing a foul-smelling, brown, oily substance that the Allies hadn't encountered before.

- A new type of chemical attack had been unleashed. This material was not a slow, silent killer like phosgene. It was potent—so fast acting that there was no time to escape for those unfortunate enough to be in its presence.

- This new chemical weapon earned the name mustard gas, because its smell somewhat resembles rancid garlic or mustard. It was dichloroethyl sulfide, courtesy of the laboratories of Fritz Haber and the chemists at the Kaiser Wilhelm Institute.

- Mustard gas is positively horrific in its action. It does not need to be inhaled to cause severe trauma. Simple skin contact will do. Water can displace the chlorine atoms of this compound easily, creating hydrochloric acid burns just like its counterparts.



- But mustard gas doesn't just create strong acid when inhaled into the lungs like its counterparts chlorine and phosgene. Instead, it undergoes a self-cyclization reaction, forming a very unstable ring structure. This unstable molecule then reacts with the guanine residues in DNA on contact, making a chemical bond to the base that prevents proper base pairing. This kind of cellular damage leads to cell death or possibly even cancer in those exposed to it.

- The effects of mustard gas on unprotected soldiers was terrible, causing thick scarring anywhere it came into contact with a victim's flesh. Thankfully, mustard gas was only developed as a weapon in the waning months of World War I, so its use in battle was very limited. But it had already done its job of wreaking terror on soldiers on both sides of the conflict with its terrible, disfiguring results.

- Although chemical weapons resulted in only about 3% of deaths in the war, they were still among the most reviled and feared weapons in use. By the war's end, more than 100,000 tons of chlorine, phosgene, and mustard gas had been produced and used on the battlefields.

ZYKLON B

- Hydrogen cyanide is a very simple molecule, yet a very potent poison. Discovered in the 1800s, in the right concentrations, hydrogen cyanide gas can be extremely lethal. When this weak acid dissociates, its conjugate base—a cyanide ion—looks desperately for a new bond to form to reduce its negative charge.

- When inhaled, hydrogen cyanide quickly makes its way into a person's bloodstream, where the pH is buffered to about 7.4 by carbonates and phosphates. With a pK_a of about 9.2, that means that only about 1% of the hydrogen cyanide that gets into a person's bloodstream becomes ionized. But that is all it takes.

- Cyanide ion bonds tenaciously to the metal centers in proteins called cytochromes—specifically, cytochrome C oxidase, which plays a critical role in transporting electrons obtained from respiration. Cyanide binds so powerfully to cytochrome C oxidase that it is effectively permanent. This causes havoc on a person's ability to process chemical energy, leading to a rapid, painful death even at very low concentrations.

- The lethality of this compound was understood in the 1800s, when it was employed as an insecticide in some applications. But hydrogen cyanide suffers from several shortcomings when used as a weapon. When released, hydrogen cyanide rises and disperses to nonlethal concentrations into the atmosphere quickly. This makes it essentially useless as a battlefield weapon.

- But Hitler's Third Reich found an even more dubious application for hydrogen cyanide than using it against troops on a battlefield. At the Auschwitz prison camp in Nazi Germany, a lieutenant colonel named Rudolf Hess, who built the now-infamous gas chambers, packaged hydrogen cyanide into canisters containing stabilizers and adsorbents to make it easier to handle and release. This new product was dubbed Zyklon B, and it is the deadliest chemical weapon ever used—responsible for the murder of about 2.7 million people.

NERVE AGENTS

- A more modern option in chemical warfare, a nerve agent known as Sarin was first discovered in 1938 by Nazi scientists seeking to develop a better pesticide. Its toxicity to humans was quickly discovered, but thankfully mass production methods were not developed until after World War II came to a close.

- Sarin is an organophosphate compound with remarkable human toxicity. It represents a turn in the philosophy of chemical warfare agents because, unlike the brute-force reactivity of its predecessors, Sarin acts on biological systems with great specificity.

- Sarin blocks the function of very specific receptor proteins that help muscles function, causing paralysis and normally suffocation in victims who cannot breathe properly as a result. With the advent of nerve agents like Sarin, the dark world of chemical weaponry started to really catch up with some of nature's deadliest chemical strategies, such as toxins and venoms.

READING

Everts, "When Chemicals became Weapons of War." http://chemicalweapons.cenmag.org/when-chemicals-became-weapons-of-war/.

Rhees, "The Chemists' War."

QUESTIONS

1. Considering that most explosive weapons also use chemical reactions to achieve their task, what is it that sets chemical weapons apart from more conventional weapons?

2. Could some of the poisons, toxins, and venoms from the previous lecture be deployed as chemical weapons? If so, what challenges would their developers face?

Tapping Chemical Energy: Fuels

LECTURE 55

From the moment that humans harnessed fire, the quest for energy was underway—and it continues to this day. Our relentless search for the energy that we need to improve our lives has led to the invention of many methods of extracting energy from our environment. Although we have devised many diverse technologies to accomplish this, they all share at least one common need: fuel, which is the subject of this lecture.

FUEL

- A fuel is any substance that releases energy, either as work or heat, as a result of a chemical reaction with an oxidizer. By that definition, just about everything around us is a fuel in one way or another, as long as a sufficiently strong oxidizer is used.

- A more convenient definition is a material that releases energy in a chemical reaction with oxygen. Because oxygen is abundant in our atmosphere, it serves as the oxidizer for most fuels with which we are familiar.

- The classic examples of fuels are those that we combust in air, and almost certainly the first of these was wood. Wood is essentially the biopolymer cellulose, which is a carbohydrate polymer. It stores great chemical potential, but it is chemically too tough for our bodies to use it as an energy source. But if that cellulose is exposed to oxygen from the air and sufficient heat, a reaction will take place. Oxygen from the air combusts the cellulose fuel, releasing large quantities of energy.

- Prehistoric and modern-day people alike have made use of this reaction for the energy needed to cook food and heat their living spaces.

- But wood is not the only fuel that has helped to shape the society that we live in today. Some archaeologists estimate that humans were using oils from the ground as fuel somewhere around 6000 to 10,000 years ago.

- By the time of the ancient Greek and Persian civilizations, a thick, black, flammable substance had been discovered and put to regular use. The Greeks called this naphtha; a more modern term is pitch. This material was used by Spartans to ignite sulfur, creating what might have been the first chemical siege weapon ever used.

- On the scale of great discoveries that changed the human world, the discovery of naphtha is just one notch lower than the discovery of fire itself—not because it burns any differently than wood, but because it is a liquid, which is more easily transported and stored because it takes the shape of its containers. Also, it can serve as a source of a number of different fuels so versatile and powerful that they serve as the basis for most fuels on which we rely even today.

PETROLEUM DISTILLATES

- But naphtha, or pitch, wasn't always the preferred fuel of humankind. Near the surface of the Earth, it is exceedingly rare to find, so even though it was useful as a fuel product, there simply wasn't enough of it to go around.

- So, humans turned to other sources of flammable liquids to use as fuels. For centuries after the discovery of naphtha, the preferred fuel for lamps and other devices requiring energy was the oil of plants and animals. Olive oil and whale oil were particularly prevalent in lighting technology from the times of ancient Greece up to the 1800s. These naturally sourced oils were a favorite for centuries because they could be collected in sufficient quantities to meet society's needs at that time.

- In today's world, the term "fuel" almost certainly conjures up images of gasoline, kerosene, diesel, and the many other classes of liquid fuels that we rely on to move our vehicles, heat our homes, and prepare food. Sometimes we turn to compressed gases as well, such as natural gas, which is essentially methane and propane.

- These fuels range from lighter-than-air methane to denser-than-air butane—from our culture's motor fuel of choice, octane, to diesel and kerosene, which can sometimes freeze on a cold winter night. As diverse as their properties are, this remarkable group of fuels all come from the same source material: petroleum.

- The creation of the petroleum that we pump from the ground and ultimately turn into the fuels that we use every day started on its chemical journey a few hundred million years ago.

- For example, Texas houses famously productive oil fields. When we think of Texas today, we usually think of dry, rugged terrain—the sort of terrain that doesn't look very conducive to the development of sea life.

- But 200 million years ago, in the Jurassic age, the land that is now Texas was an inland sea, teeming with sea life—much of it plants and microbes. When these creatures died, they sank to the seafloor and became covered with sediment.

- As biological matter decays, entombed in sediment and rock, oxygen can't get in to play a role in the decomposition like it does at the surface of the Earth.

- So, this carbon-rich matter decays, unable to form compounds like carbon dioxide as part of the process. Instead, decay products without oxygen tend to form, and among these are long-chain hydrocarbon molecules.

- So, slow, anoxic decomposition over millions of years produces underground deposits of hydrocarbon-containing material. At the same time, sea levels receded, eventually exposing the seafloor, much of which we now call Texas.

PETROLEUM REFINING

- Petroleum is a highly complex mixture of hydrocarbons and other compounds. It comes from the decay of organisms entombed in the ground, so the nitrogen, sulfur, and other elements that made up those organisms were trapped, too.

- Entrepreneurs of the late 1800s discovered that petroleum could be separated into materials of differing volatility through distillation, which can be used to separate hydrocarbons based on their volatility, which is closely related to their molecular size and shape.

- This process can be used to collect natural gas, which is primarily methane, and other familiar flammable gases like propane and butane—as well as some familiar liquid fuels like gasoline, comprised of hydrocarbons with about 5 to 12 carbons per molecule, or diesel and kerosene, each made from hydrocarbons of about 10 to 15 carbons per molecule.

- Petroleum distillation was a very effective technique for producing usable fuels from complex petroleum mixtures—at least at first. When used as a lamp oil or a heating fuel, only a certain level of purity is needed. Even in its earliest forms, kerosene seemed downright pure compared to the messy, sometimes smelly, whale oil alternative.

- But modern engines and other devices require more refined fuels, both for more predictable combustion properties and for cleaner operation. As millions and millions of people began relying on fuels like gasoline and diesel to move our vehicles, it started to become necessary to get some of those uninvited guests in our fuels out.

- One of the most undesirable visitors in our most popular fuels is the element sulfur. The production of sulfur oxides that would have been released into the environment are largely avoided through the process of desulfurization.

- The downside to this process is that it produces a tricky product of its own: dihydrogen sulfide. Weakly acidic, with a pK_a of around 7, dihydrogen sulfide can react with many metals commonly used in the construction of desulfurization reactors.

- Iron can be oxidized by protons from the protons of acids. In this case, the oxidized iron combines with the sulfur removed from the fuels to create iron sulfide, a weak brittle material that is purged from the reactor lines by moving gases as it forms.

ISOMERIZATION AND OCTANE RATING

- Diesel fuel isn't the only type of petroleum distillate that requires chemical treatment before it makes it to your local filling station for use in your vehicle. Gasoline also undergoes additional chemical treatment after distillation to improve its performance in engines.

- Gasoline engines in particular can be very fussy about the exact detonation properties of the fuel that they use. This means that even from one gasoline engine to another, different formulations of gasoline are necessary for proper performance.

- Gasoline engines, unlike their diesel counterparts, rely on a spark from a spark plug to achieve detonation. An engine cylinder is filled with a gas-air mixture and then compressed by a piston prior to detonation. A spark initiates combustion of the fuel at just the right time, and the resulting expansion pushes the piston back to complete the second stroke of the 4-stroke sequence.

- The potential problem is that compressing a hot mixture of gas and air can increase its temperature and cause detonation before the first stroke of the piston is complete and the spark plug fires. This causes the engine to malfunction and possibly even become damaged.

- The solution to this problem is to use fuels that are adequately resistant to detonation under the heat and pressure conditions that a particular engine generates. The more branched a hydrocarbon is, the more resistant to detonation it will be.

- The compounds that make up gasoline, primarily hydrocarbons from 5 to 12 carbons in length, are often passed through special reactors with metal catalysts designed to promote isomerization reactions that lead to more branched products.

- But that leaves the question of how to report on the detonation resistance of the fuel blends before and after the isomerization process. The system that is used compares the detonation resistance of the product to that of single pure hydrocarbon materials, resulting in an octane rating.

- The detonation characteristics of motor fuels are so important that many additives have been tried over the past century to alter this characteristic. A modern additive used to reduce premature detonation of fuels is methyl tertiary-butyl ether (MTBE), which delays combustion to the appropriate time.

BIODIESEL

- Petroleum products have undoubtedly changed the world and how we obtain energy. Since the discovery of petroleum in the 1850s, it has been the go-to fuel for vehicles, furnaces, and more.

- But it takes petroleum millions of years to form underground, and it has taken us just a few centuries to put a serious dent in the global supply. Because we use petroleum at a pace about 10,000 times faster than it can form, there is a serious gap in the renewability of this critical energy source.

- In the past few decades, this notion has led many to consider what will happen if oil becomes too scarce or expensive to produce for the world's energy needs. When and if we will ever run out of petroleum is a very difficult thing to predict, because new deposits are always being located and newer technologies continue to make previously inaccessible or unrecoverable deposits available to us.

- Even so, when it comes to something as critical as world energy supply, it makes sense to think ahead and be ready with alternatives when and if oil can't fulfill all of our energy needs.

- One very attractive alternative to petroleum products is biodiesel, which is created from the natural plant oils extracted from growing plants. That means that we can grow a field of raw material to make biodiesel in a single growing season, instead of having to wait an entire geological era, as we do for petroleum.

- A simple process converts the large, viscous fats from plant oil into molecules that are strikingly similar to—and can be used essentially interchangeably with—the hydrocarbons found in diesel fuel. This amazing product can be used in many standard diesel engines without further modification to the engine itself.

READING

Stein and Powers, *The Energy Problem*, chaps. 5 and 7.

UC Davis ChemWiki, "15.11 Fossil Fuels and the Energy Crisis." http://chemwiki.ucdavis.edu/ChemPRIME/15Thermodynamics%3A_Atoms%2C_Molecules_and_Energy/15.11%3A_Fossil_Fuels_and_the_Energy_Crisis.

QUESTIONS

1. Considering that octane ratings convey information about detonation resistance in gasolines and the fact that gasoline engines use a spark plug to initiate combustion, are there any potentially problematic consequences of using high-octane fuel in a low-compression engine? What about using low-octane fuel in a high-compression engine?

2. The production of biodiesel requires not only triacylglycerides from plants, but also methanol. What are some sources from which we might obtain methanol?

Unleashing Chemical Energy: Explosives

LECTURE 56

In this lecture, you will learn about one of the most influential chemical inventions of all time: explosives, which are materials that release their energy not evenly and slowly, but in a violent event that can be harnessed to do immense good or catastrophic evil. You will discover how conventional explosives—including gunpowder, guncotton, nitroglycerin, picric acid, trinitrotoluene (TNT), and plastic explosives (such as C4)—were discovered and how they have impacted human history.

GUNPOWDER

› In China, as early as the 1st century A.D., the medicinal value of a class of chemical compounds known as nitrates was realized. Healers of that great culture used nitrates to treat heart ailments, realizing that ingesting small quantities of this material improved circulation and eased chest pain.

› After several hundred years, physicians were experimenting with a new concoction of remedies, mixing potassium nitrate with charcoal and sulfur. But by combining potassium nitrate—a strong oxidizer—with charcoal—a good fuel, they were truly playing with fire. Add a pinch of sulfur, which can accelerate the reaction, and this experimental medicine, both figuratively and literally, blew up in their faces.

› Gunpowder had been created for the first time, and it was quickly realized that this combination of materials was not suitable for medicinal use. But it was suitable for a very different use: releasing large amounts of stored chemical energy in an instant.

- The chemical reaction that drives gunpowder explosions—specifically, black powder explosions—is carbon with potassium nitrate and a little bit of sulfur to lower the energy needed to start the reaction.

$$3\ C\ (s) + 2\ KNO_{3\ (s)} + S_{\ (s)} \rightarrow 3\ CO_{2\ (g)} + N_{2\ (g)} + K_2S_{\ (s)}$$

- When 3 moles of carbon are mixed into a black powder mixture and then combusted, about 600 kilojoules of heat are liberated at standard temperatures. Add to this energy release the fact that it happens very quickly—and that all-solid ingredients react to form carbon dioxide and nitrogen gases, causing expansion—and you have one very hot, forceful expansion as a result of this reaction.

- This force is adequate to propel rockets across the sky, or musket balls across a battlefield, and it remained the method of choice for this purpose from the time of its invention until the late 1800s.

SELF-OXIDIZERS

- Black powder, though ingenious for its time, still technically requires the mixing of fuel and oxidizer. Of course, both are in the solid phase, so grinding them together into a fine powder can make for one very fast reaction and release of energy.

- But no amount of grinding can mix fuel and oxidizer as closely together as chemically bonding them one to the other can. And although it took some time—about 8 centuries after gunpowder's development—a technique for this was eventually developed.

- Credit for the discovery often goes to Christian Friedrich Schönbein, in 1845. A decade earlier, it had been realized that mixing the cellulose from wood with nitric acid formed some remarkably flammable products. Schönbein discovered that the same effect that had been observed using the dense cellulose of wood was amplified when lighter cotton fiber—made of the same cellulose material—was substituted. The resulting compound was called guncotton, and it combusted with remarkable vigor.

- Guncotton's chemical name is nitrocellulose, which contains unstable nitrate groups and lots of oxygen. The detonation of nitrocellulose trades very unstable nitrate groups for very stable nitrogen gas and carbon dioxide.

$$2\ C_6H_7N_3O_{11} \rightarrow 9\ CO + 3\ CO_2 + 7\ H_2O + 3\ N_2$$

- When we combust 2 units of nitrocellulose, we get 9 moles of carbon monoxide, 3 moles of carbon dioxide, 7 moles of water, and 3 moles of nitrogen gas—all of which are stable compounds that release lots of energy when they form, except for carbon monoxide gas.

- Nitrocellulose combusts well, but it needs more oxygen to completely combust carbon monoxide to carbon dioxide. As a result, it doesn't release quite as much energy as it could. In other words, although it is a self-combusting material, it's not optimized yet.

- The cleaner burning nature and easy synthesis of guncotton caused it to quickly replace gunpowder in most firearms applications. But the quest for a fully self-oxidizing compound continued. And it wasn't long before an Italian chemist named Ascanio Sobrero produced the first completely self-oxidizing compound.

- Sobrero used nitric acid to convert glycerin, a readily available material that is a by-product of the soap-making process, into an explosive of legendary power called nitroglycerin.

$$4\ C_3H_5(ONO_2)_{3\ (l)} \rightarrow 12\ CO_{2\ (g)} + 10\ H_2O_{\ (g)} + 6\ N_{2\ (g)} + O_{2\ (g)}$$

- In this reaction, the glycerin molecule reacts with nitric acid in a condensation reaction, expelling some water and creating nitroglycerin. This particular compound has loads of oxygen—enough to completely get the job done of self-oxidizing.

- In this reaction, there's no carbon monoxide left; nitroglycerin has oxidized completely. In fact, it's oxidized so completely that there's actually a little bit of oxygen left over. This is what makes nitroglycerin such an effective and potent explosive.

- Sobrero found nitroglycerin to be highly unstable. In its pure state, it could be made to detonate by the heat generated by a single candle or a physical shock as mild as dropping a container from the lab bench to the floor. Sobrero became a vocal critic of his own creation. But a contemporary of his felt differently.

- The now-famous Alfred Nobel worked to find a way to stabilize nitroglycerin, making it safer to transport and set up before releasing its awesome destructive force. He discovered that he could use a mineral compound called diatomaceous earth—an inert, crumbly, powderlike material that the liquid could adhere to, creating a more stable material that could be fashioned into sticks and wrapped in paper to produce a product that would not detonate if dropped or left in the Sun. It delivered no less energy on detonation but simply required a stronger shock to set it off.

- Nobel proved to be a prolific inventor and businessman, developing a blasting cap—a special detonator used to deliver that shock to his dynamite. This and 354 other patents made Nobel a very wealthy man by the time of his death in 1896, before which he established what is arguably the most distinguished award that a chemist can receive: the Nobel Prize.

PICRIC ACID AND TNT

- Yet another popular explosive from that era was picric acid, a compound that is synthesized by reacting a compound called phenol, which is easily extracted from coal tar, with nitric and sulfuric acids. The product of this reaction is picric acid, an extremely powerful and very shock-sensitive reagent.

- Picric acid and nitroglycerin have some similar-looking functional groups, but picric acid is a larger molecule and exists as a solid at room temperature. And that solid, when kept dry, explodes just like nitroglycerin, at the slightest shock.

- Picric acid, the explosive of choice in World War I, is a chemical cousin of one of the most famous explosives in the world today: trinitrotoluene (TNT). First synthesized in the 1860s, TNT was used primarily as a dye because of its attractive yellow color. It was not until 2 decades later that its explosive properties were fully understood and explored.

- TNT has 2 very important differences when compared to picric acid. First, it is a bit more difficult to detonate, which makes TNT compare to picric acid in much the same way that dynamite does to nitroglycerin. Second, substitution of a methyl group for the hydroxyl of picric acid makes TNT unable to hydrogen bond to other TNT molecules. This lowers the melting point of TNT in comparison to picric acid, so TNT could be melted down easily and poured into artillery shells in its safer liquid form.

- TNT was adopted by the German military prior to World War I with striking results. In a counterintuitive twist, the greater resistance to detonation made TNT a more damaging weapon. Shells filled with TNT had that extra fraction of a second to penetrate armor before exploding, whereas shells using picric acid tended to explode instantaneously on the slightest contact with their target.

- These favorable characteristics of TNT, though not recognized immediately by all nations, have since made it an ordinance of choice for militaries around the world.

PLASTIC EXPLOSIVES

- Plastic explosives are most simply defined as explosive materials that are moldable. They are particularly useful in demolitions applications because their soft form allows them to be very precisely placed and shaped to effect maximum destruction with minimum explosive power.

- Although plastic explosives like the famous C4—used by militaries and even terror organizations across the globe—are relatively recent inventions, their history reaches back more than a century, all the way to Alfred Nobel.

- Nobel always struggled with a serious problem with dynamite: Liquid nitroglycerin was sweating out of the dynamite over time, leading to potentially deadly pools of nitroglycerin forming in crates of his high explosive.

- In light of this problem, Nobel started to seek out new materials to replace the diatomaceous earth that he had originally used to produce dynamite. He turned to an absorbent that was not inert, but explosive in its own right, to stabilize the nitroglycerin: guncotton. In 1875, he perfected his recipe, creating a sort of explosive gel comprised of nitroglycerin, guncotton, wood pulp, and a few other ingredients.

- The resulting product was a gelatin-like substance with explosive power greater than nitroglycerin, but with greater stability and less propensity to sweat nitroglycerin. As a bonus, it was easily moldable into the needed shape at the time of use.

- More modern versions of plastic explosives have a more obvious connection to their name. C4, for example, does in fact contain plastic—just a small amount, though. C4 consists of about 2% to 3% polyisobutylene, an addition homopolymer that also has been used as a base for chewing gum.

- The difference between C4 and chewing gum is that instead of being mixed with colors and flavoring, the polyisobutylene in C4 is instead laced with a massive amount of a compound called 1,3,5-trinitroperhydro-1,3,5-triazine, more commonly called research development explosive (RDX). The structure of RDX has stability-stealing formal charges on nitrogen and oxygen in abundance, making a self-oxidizing compound with highly explosive properties.

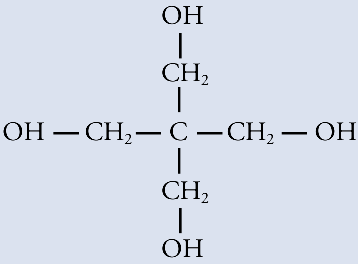
READING

Brown, *The Big Bang*.
Walker, *Blizzard of Glass*.

QUESTIONS

1 For explosives to be effective, the energy released must be transmitted through shock waves. How might a conventional explosion taking place in space appear different to one taking place on Earth? Would you expect it to be as destructive?

2 Pentaerythritol tetranitrate (PETN) is one of the most explosive substances ever created by humans. It is formed in a reaction similar to that used to make nitroglycerin, but pentaerythritol is used as the starting material instead of glycerin. What is the chemical structure of PETN?

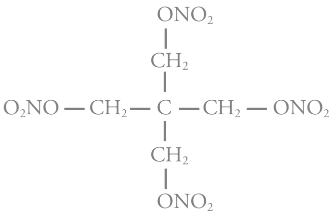


$$\begin{array}{c} & & & & OH & & & & \\ & & & & | & & & & \\ & & & & CH_2 & & & & \\ & & & & | & & & & \\ OH & - & CH_2 & - & C & - & CH_2 & - & OH \\ & & & & | & & & & \\ & & & & CH_2 & & & & \\ & & & & | & & & & \\ & & & & OH & & & & \end{array}$$

(Pentaerythritol)

Answer

2)



$$\begin{array}{c} & & & & ONO_2 & & & & \\ & & & & | & & & & \\ & & & & CH_2 & & & & \\ & & & & | & & & & \\ O_2NO & - & CH_2 & - & C & - & CH_2 & - & ONO_2 \\ & & & & | & & & & \\ & & & & CH_2 & & & & \\ & & & & | & & & & \\ & & & & ONO_2 & & & & \end{array}$$

Chemistry of the Earth

LECTURE 57

This lecture is about geochemistry. Geology is the study of natural Earth systems, and geologists try to understand the properties and interactions of materials within a planetary body—usually our Earth. But just like all other forms of matter, rocks and minerals also fall into the domain of the chemist, and it is often the chemical composition of these rocks and minerals that dictates their behavior in natural systems, impacting how mineral deposits form, volcanoes erupt, or tectonic plates move. In this lecture, you will discover how chemistry drives the magnificent machine that is our planet.

COMPOSITION OF THE EARTH

- About 4.5 billion years ago, when the Earth was just forming, chunks of debris from the proto–solar system were on the move, colliding with one another to create large masses. These larger masses created gravitational eddies that drew in more and more mass, ultimately creating planets. This process is commonly referred to as accretion and is generally accepted as the mechanism by which the Earth formed.

- Over several hundred million years, more than a trillion trillion kilograms of material collided and smashed together to form the mass of material that was destined to become Earth. All of those impacts carried with them great energy, which, through a combination of pressure, friction, and radiation, produced a rather hot planet—so hot that it was entirely molten.

- In this hot, liquefied state, over geological timescales, the Earth slowly began to sort itself out by density. Iron and nickel, most notably, sunk to the dense, metallic core of the planet. Lighter but still abundant metals like aluminum and magnesium, silicon, and oxygen instead rose to the outer regions of the planet, forming the mantle and crust.

- Geologists call this process differentiation, and it led to a planet of nonuniform consistency that is organized into layers with drastically differing properties.

INNER AND OUTER CORES

- Differentiation's effects reach all the way to the core of the planet. Nickel, being a bit denser than iron, is thought to be the primary component of the inner regions of the core.

- This creates a very interesting situation, because nickel has a higher melting point than iron, and it turns out that the pressure and temperature conditions at the core—about 3.5 million atmospheres and 6000° kelvin—are just such that the nickel inner core remains solid while the outer iron core is molten.

- We know that the inner core is solid and the outer core is liquid because of the way that they transmit seismic waves created by earthquakes, volcanic eruptions, and even nuclear bomb tests.

- Beginning with this constraint, scientists then calculate the pressure at the center of the Earth using information about its radius and mass. Under that pressure, maintaining liquid iron and solid nickel can only be accomplished under a specific range of temperatures—temperatures close to those present on the surface of the Sun.

- Having a partially molten core is a rather fortunate structural feature of the Earth. Although not much more is known about exactly how the core behaves, it definitely has an observable effect both at and even above the Earth's surface.

- The molten outer core decouples the core from the rest of the planet, allowing motions within these layers, driven by the heat of radioactive decay of heavy elements. These motions in the iron- and nickel-rich layers create a magnetic field. This field extends far beyond the surface of the Earth, protecting us from harmful radiation from the Sun and other cosmic rays. It also maintains a fairly constant orientation, helping us navigate the globe.

THE MANTLE

- The vast remainder of the Earth outside of the core is solid rock. In fact, all but the top 400 miles or so of what is known as the mantle is rigid, unmoving rock. By "rock" we mean a collection of silicate minerals—metals blended with silicon and oxygen in different proportions to create distinct minerals with varying properties.

- The phase behavior of silicate minerals is quite complex. But as a general trend, silicates that are rich in magnesium and iron (sometimes called mafic silicates) tend to be slightly denser and have slightly higher melting points than do those rich in aluminum, potassium, and sodium (sometimes called felsic silicates).

- Just as with the core, as we move upward through the mantle, its composition changes, taking on more and more felsic composition and less and less mafic composition until it reaches a critical point where the mantle isn't really all that solid anymore. The lower melting point of the felsic material makes it slightly plastic, or able to flow over a narrow, several-hundred-mile span of depths just below the crust of the Earth.

- The mantle is separated into a tough, rigid higher iron-and-magnesium portion called the mesosphere and a weaker, mushier plastic region called the asthenosphere. The existence of the asthenosphere is critical to the geology of the Earth's surface. Without it, plate tectonics would not exist, and what we have come to know as a slowly changing landscape at the surface, with drifting and sometimes colliding continents, would be very different.

THE CRUST

- The final geological layer is the crust of the Earth—the outer layer of solid material that we call home. Although the term "crust" might invoke thoughts of very thin layers, the Earth's crust is, in fact, the only region of our planet that humans have ever directly explored.

- Our characterization of the core and mantle layers have all been determined not by direct observation, but by inference from seismic data and samples brought to the surface by geological processes like volcanoes.

- The crust, like the mantle, has a great deal of silica, but the identities and ratios of the accompanying metals are very different. Crustal rock is richer in aluminum, potassium, and sodium because the silicate minerals that they comprise are generally just a bit less dense than others. There is still some magnesium and iron, but in less abundance than in mantle rock.

- Just as with the other regions of the Earth, we tend to find less dense materials higher up due to the process of differentiation. Continental crust is largely lighter-colored, less-dense felsic minerals like quartz, muscovite, and feldspar, while the crust of the ocean floor is more mafic in nature, comprised mostly of darker, denser minerals like olivine and pyroxene.

PLATE TECTONICS

- Planetary accretion over hundreds of millions of years created this grand layered structure of the Earth, which we can rationalize based primarily on the settling of materials due to density early in Earth's life. But our generally sound method of reasoning the Earth's structure by density starts to fail on closer inspection of more confined regions.

- For example, French scientist Alexandre Brongniart noted in the early 1800s that unusually dense iron-and-magnesium–containing mafic rocks could be found in certain regions of the Alps. His discovery meant that there had to be something more than just density dictating the composition of our planet, and it foreshadowed the greatest shift in the history geological theory—that of plate tectonics.

- Until only a few generations ago, it was widely assumed that the surface of the Earth was a rigid, static, unchanging thing—that continents were in positions fixed since the creation of the globe.

- But the theory of continental drift, first advanced in 1912, challenged that old assumption and prompted geologists to contemplate the possibility that the continents actually moved across the globe and relative to one another painfully slowly, just a few centimeters per year, but enough to alter the face of the Earth over extremely long time periods.

- So, the theory of plate tectonics, an explanation in which continents and seafloors form plates with defined boundaries, was developed. These plates ride along on thermal currents in the soft, plastic asthenosphere, and at their boundaries, the plates can spread apart as they do at the center of the Atlantic Ocean, crash into one another as India and Asia do today, or slide along one another laterally as they do at the San Andreas Fault in California.

- This model works remarkably well to describe why we see anomalies in the locations of rocks, as Brongniart observed. It also helps us explain why certain volcanoes erupt so differently. The accumulation of less-viscous magmas that are richer in magnesium and iron lead to long, lazy eruptions like Mount Kilauea in Hawaii, which is currently undergoing an eruption that started in 1983. This makes sense, because Kilauea is over a hot spot in the middle of the ocean, whose floor is made from iron-and-magnesium–rich rock.

- But the much higher viscosity of felsic magmas is created in areas called subduction zones, where continental rock is colliding with seafloor. The seafloor slides under the felsic rock of the continent, but it also drags down some of that continental material with it. This fills magma chambers with thick felsic magma that resists flow. This magma acts more like a plug, building pressure in the magma chamber until it is released explosively, as was the case on August 27, 1883, on the island of Krakatoa, which essentially exploded in a series of 4 massive volcanic eruptions.

- All of this grinding, colliding, and diverging over billions of years can cause rocks of greater density to be lifted up, and sometimes even onto less-dense ones. It can cause processes that mix silicates of differing composition in magma chambers beneath the surface.

- Plate tectonics explains why Brongniart and others observed what appeared to be ocean floor–like minerals high in the Himalayas, and it explains why each volcano around the world seems to have an eruptive personality all its own. But where is the energy to move and mix all of that material coming from?

- Some heat was trapped during the initial cooling of the Earth as it formed, but to drive an engine so massive and powerful that it can move not only mountains, but also whole continents, there must be a fuel source that continuously provides slow, steady heat release over time.

- The source of the energy that created the Himalayas and the Rocky Mountains, that shrinks and grows oceans, and even that drives titanic volcanic explosions is the atom.

- It has been estimated that about half of the thermal energy given off by our planet is due to radioactivity in heavy elements trapped beneath its surface. Radioactive elements deep within the mantle of the Earth, trapped at the time of its formation, have been decaying and will continue to slowly decay, releasing a small fraction of their mass energy in the form of heat that drives the grand machine that is our planet.

- Mostly, trapped uranium-238 is what we have to thank for this. This dense radioactive element accumulated in silicate minerals in the mantle about 4.5 billion years ago as the Earth accreted and cooled. And there it rests—at least about half of it, because uranium-238 has a half-life of just about 4.5 billion years.

- As this element continues to undergo slow alpha decay, it will continue to emit a large fraction of the heat that drives convection in the asthenosphere. In essence, we are all riding through space on a gigantic nuclear power plant.

READING

Middlemost, *Magmas, Rocks and Planetary Development*, chaps. 1 and 2.

UC Davis GeoWiki, "2.2: Structure of the Earth."
http://geowiki.ucdavis.edu/Core/Oceanography/02%3A_Earth%3A_Formation_and_Structure/2.2%3A_Structure_of_the_Earth.

QUESTIONS

1. How might water near the surface of the Earth play a role in the transportation and accumulation of certain elements and minerals?

2. Much of what we know about the Earth's subsurface is determined from indirect observation. What sort of challenges would be faced by a project to drill to the core of the planet? Do you think that humanity ever will, or ever should, make an attempt?

Chemistry of Our Oceans

LECTURE 58

Water is critical to the creation and evolution of life on our planet. In this lecture, you will consider the roles played by the greatest depository for water on our planet—its oceans—and how they behave at the molecular level. Oceans make up 75% of the surface of our planet, and the chemistry that goes on within the oceans can be used to create products such as fuel, clean drinking water, and more.

COMPOSITION OF THE OCEAN

- The ocean spans quite a significant volume of space. With a surface area of 129 million square miles, a maximum depth of about 6 miles, and somewhere around 200,000 miles of shoreline, the Earth's oceans are a vast and complex chemistry lab.

- By mass, our oceans are about 97% water, but the remaining 3% or so is made up primarily of dissolved ions. Nearly all of the salt content of ocean water is comprised of just 6 ions: Chloride and sodium make up the lion's share of the dissolved ions, with some magnesium, sulfate, calcium, and potassium as well. In general, these proportions of ions in seawater are remarkably constant across the globe.

HYDROCARBONS FROM THE SEA

- Natural gas is usually associated with the subsurface of terrestrial locations. It is a product of petroleum distillation and is one of the cleanest-burning hydrocarbon fuels available to us.

- But in the 1930s, as use and transportation of methane, the principal component of natural gas, increased, a problem was discovered. Pipeline workers began complaining of clogs forming in high-pressure gas lines in colder regions. It seems as though there was some moisture in the lines that was freezing, causing the clogs to form.

- An investigation led scientists to the realization that the material clogging the line did in fact contain frozen water, but it was not your everyday ice. This ice had methane molecules trapped within a molecular cage of frozen water.

- The phenomenon of trapping single molecules inside crystals of ice had already been observed. Michael Faraday had reported on this phenomenon happening with chlorine and water as early as 1823, more than a century earlier. Faraday had named the compounds clathrates, from the Latin term *clathratus*, meaning "cage"—inspired by the imprisoned molecules isolated within their jail of crystalline water.

- Pipeline engineers went about trying to find a way to break up or prevent the formation of these newly discovered methane clathrates, considering them a nuisance and an obstacle to their mission of delivering their natural gas product.

- But that attitude changed in the 1960s, when methane clathrates were discovered naturally occurring in permafrost in Siberia.

- Several decades of prospecting led to the realization that methane hydrates are not just a pipeline nuisance or even a curiosity that forms in the most frigid parts of the world. They occur in many regions around the world under the sea.

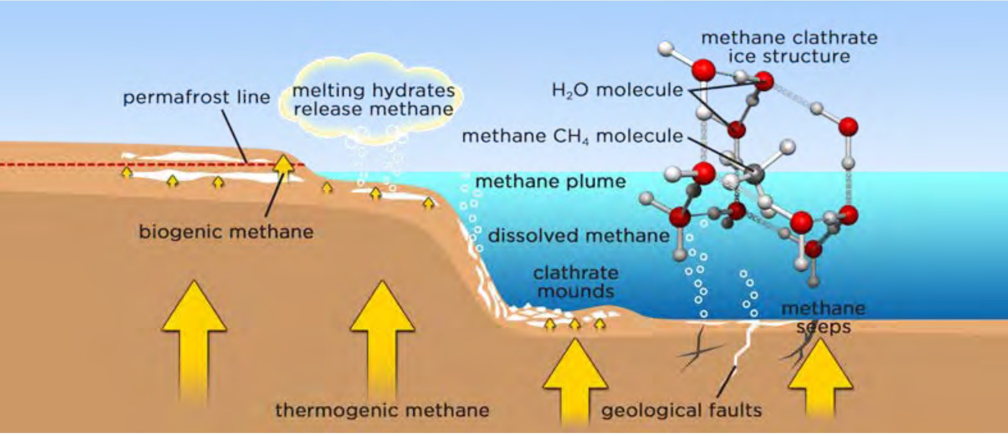
- Methane hydrates require a few things to form. The presence of methane and water are prerequisite, and because methane hydrates are solids, we expect them to form under conditions of high pressure and low temperature—such as the conditions found at the bottom of the ocean.

- Since the first discovery of seafloor methane hydrates in the late 1980s, prospectors have found deposits on the shallow continental shelves of every continent. But they are not commonly found in the deep ocean, where the pressure is greatest.

- This is because the most basic criterion for the formation of methane hydrates is methane. Careful testing of methane from natural hydrates, using sophisticated mass spectrometers, has revealed that the methane contains just a slim fraction more carbon-13 than one would expect based on this isotope's overall abundance in nature.

- This told scientists that the methane was created biologically. Because carbon-13 is processed slightly slower in biochemical reactions, it tends to accumulate in living things. And this signature pointed to bacteria producing the methane found in seafloor hydrates.

- Bacteria that live in the sediments on continental shelves consume organic matter as it falls to the seafloor. These bacteria have a special metabolism that produces methane as a by-product of their biochemistry. Called methanogens, these bacteria are responsible for the methane-rich layers found in the rocks around them.



- The amount of methane trapped in hydrates is not well known, and it's still debated just how much might be down there, waiting to be released. Even conservative estimates, however, hint that there is more carbon mass locked in seafloor hydrates than there is contained in all the world's coal and petroleum reserves combined.

- Hydrates could change the world for the better by offering a new source of energy to help power the world. But there may be a much darker side to these deposits.

- Methane hydrates tend to form on continental shelves, near areas where ships and planes most frequently travel. Some theorize that the sudden, massive release of methane gas into the ocean by unstable clathrates might help explain why some ships mysteriously sink in these regions. It is an intriguing theory, but one that has yet to be confirmed by direct observation.

- Sudden methane release has the potential to have global effects, because it is a greenhouse gas. Methane absorbs infrared radiation and acts like a blanket to our planet, increasing atmospheric temperatures when it accumulates. So, releasing additional methane into the air can contribute significantly to the increasing global temperature.

- Methane hydrates aren't that stable, even where they have formed underwater. Sometimes just a slight agitation by an earthquake or gentle heating by a warming ocean current can change conditions around hydrates and make them suddenly unstable.

- Climatologists and geologists widely agree that spontaneous decomposition of hydrates might be a major contributor to global warming events.

- The warming of the planet and its oceans triggers the release of large amounts of methane from hydrate deposits, resulting in the buildup of methane in the atmosphere. This methane buildup promotes additional warming, which promotes additional hydrate decomposition, and a potentially devastating feedback loop can ensue.

- Such a loop might have already occurred once during the largest mass extinction our planet has ever encountered, the Permian extinction about 252 million years ago, during which as many as 96% of all species on Earth were eradicated.

- Whether we use them for our own purposes—as a source of fuel, for example—or simply try to understand their phase behavior to better protect ourselves from catastrophic environmental changes, methane hydrates are important to all of us.

CARBON DIOXIDE IN MARINE ENVIRONMENTS

- Carbon dioxide is one of the most stable gases known. It forms quite easily during the combustion reactions that go on in our cars, during respiration that keeps us alive, and during the decay of most organic matter. It is an inescapable fact of living in an oxygen- and carbon-rich environment like the one we enjoy every day.

- We often think of carbon dioxide in natural systems as a problem, in part because we humans create so much of it that we sometimes upset nature's chemical balance. Although the carbon dioxide that we generate can cause environmental problems, the presence of carbon dioxide in natural systems is also natural and, it turns out, necessary.

- Carbon dioxide is important to us as a buffer in our bloodstreams, and the same type of chemistry is also crucial to our oceans.

- Before the industrial era, the pH of the world's oceans was about 8.2. At this pH, the ocean is able to dissolve a great deal of carbon dioxide as carbonate ions. Many organisms rely on those carbonate ions as a material to create the essential corals and shells that they need to survive.

- Carbon dioxide gas in our atmosphere can dissolve into the ocean, and Henry's law predicts that as the partial pressure of carbon dioxide in the atmosphere increases, its solubility in the oceans should increase proportionally.

- So, what's the problem? How does increasing the amount of dissolved carbon dioxide in the oceans reduce the availability of essential carbonate ions that so many marine creatures depend on?

- Over time, as we continue to burn fossil fuels, we introduce more and more acid into the environment. As that acid begins to change the pH of the oceans, bringing it down, we anticipate that the equilibrium will shift. Specifically, at the pH that we're down to now—about 8.1—we have lost almost a quarter of the carbonate that was previously dissolved in the oceans simply because of the pH affecting the equilibrium.

- In the next century, experts say that the pH of the world's oceans will drop by almost another half of a pH unit, resulting in a 4-fold decrease in dissolved carbon present as carbonate ions in the oceans from the pre–Industrial Revolution values. Dropping the carbonate ion concentration that much is potentially dangerous.

- Le Chatelier's principle is driving the chemistry of our oceans. As the proton ion concentration increases as a result of human activity, the equilibrium shifts in a way that relieves that stress, consuming carbonate ion and forming more bicarbonate ion, which can't be used in the same chemical processes that carbonate ions are.

- Once this concentration reaches a critical level—one that we can't predict—then the biosphere becomes more chaotic. A number of marine organisms won't be able to survive if we continue driving down the ocean pH's the way that we have in the last century.

- As human activity pushes atmospheric carbon dioxide levels higher than normal, the ocean dissolves a sizable fraction of that carbon dioxide in accordance with Henry's law, potentially creating an environmental change so drastic that coral reefs and shellfish simply cannot adapt. There is no simple solution to this problem except for changing our habits as a species and the amount of carbon dioxide that we pump into our atmosphere.

READING

Brown, LeMay, and Bursten, *Chemistry*, pp. 785–790.

Emerson and Hedges, *Chemical Oceanography and the Marine Carbon Cycle*, chap. 4.

UC Davis GeoWiki, "14: Special Topics -- The Ocean in a Warmer World." http://geowiki.ucdavis.edu/Core/Oceanography/14%3A_Special_Topics_--_The_Ocean_in_a_Warmer_World.

QUESTIONS

1 The vastness of our oceans makes them a tempting potential source for resources other than Haber's gold. What other valuable materials might seawater be able to provide?

2 Aside from sequestering carbon for shells, in what other ways might life be affecting and even controlling the chemistry of our oceans?

Atmospheric Chemistry

LECTURE 59

Though incredibly powerful, forces such as time and chemical energy that act on the planet—altering the composition and behavior of the land, sea, and subsurface of the Earth—tend to fuel processes so slow that they are difficult to observe in a human lifetime. But as we move into the gas phase and begin considering how and why our atmosphere behaves, processes can take place much more rapidly. This lecture will dive into the chemistry of this relatively small slice of our environment.

COMPOSITION OF THE ATMOSPHERE

› Our atmosphere, much like our oceans, is relatively uniform. It has undergone some significant changes over geological time, such as the slow conversion from reducing to oxidizing conditions, but over the past few billion years, very little has changed. Once the major transition to an oxidizing atmosphere was complete, courtesy of the evolution and growth of bacterial organisms, it has remained remarkably steady.

› Our atmosphere is comprised primarily by just 2 gases: molecular nitrogen, making up about 78%, and molecular oxygen, making up about 21%. Just about anywhere you go on the surface of the Earth, you will find this ratio of nitrogen and oxygen.

› Nitrogen is essentially inert. In the case of the atmosphere, we can usually think of it as little more than a solvent, diluting the other gases that drive the chemistry of the atmosphere. Oxygen plays a role in many processes and is always present as well, at least in recent geologic time.

- But it is that remaining 1% that really spices up the chemistry of the atmosphere. After centuries of study, humankind has come to understand the powerful and complex chemistry that goes on in the atmosphere, and much of it is driven by those few remaining gases that make up the balance.

- Water vapor is special because of how rapidly and widely its concentration can change. Because the boiling point of water is so close to the temperatures that we encounter on Earth, minor fluctuations in air temperature can have a significant effect on how much water vapor the air can hold.

- Carbon dioxide is also a changing component of the air around us. Somewhat different than water, carbon dioxide levels rise and fall over much longer timescales, affected by seasonal plant activity and human use of fossil fuels over the years.

- Other gases that find their way into our atmosphere include sulfur dioxide and nitrogen oxides, which can be released into the air via coal-fueled industrial plants or from geological sources, such as volcanic eruptions or even lightning strikes. These gases tend to react on release and don't have an opportunity to spread globally, instead altering the chemistry of smaller pockets of the atmosphere, sometimes with significant consequences.

ATMOSPHERIC LAYERS

- As the 1800s came to a close, many curious researchers were out to discover what secrets lie just above our heads in plain sight, but out of reach. One of the first was Léon Teisserenc de Bort. In the latter half of the 1890s, de Bort launched hydrogen weather balloons from the weather station that he founded in Trappes, France, just outside of Paris.

- His balloons were carried aloft by the buoyancy of hydrogen and armed with a clever mechanical device designed to tear the base of the balloon after an amount of time, sending it back to Earth using the top of the balloon as a parachute to slow descent and protect its payload.

- Its payload was bottles designed to trap samples of the air aloft as well as some of the first self-recording instruments. De Bort set out to measure values like humidity and composition, which could be determined by analyzing trapped samples after the flight. But other parameters, including temperature—the data that would earn him immortality in meteorological science—were a bit trickier.

- Temperature had to be measured during the flight, so his balloons carried a cleverly designed thermometer made of various metal wires, each of which expanded and contracted in response to temperature. By attaching these wires to a pen, his thermometer would automatically record the temperature as a trace created by the moving pen. This trace would then be reviewed after the balloon was retrieved.

- Though very simple, de Bort's temperature data were fascinating. Initially, he found that temperatures gradually and steadily dropped with higher altitude. But as his balloon flights exceeded altitudes of 10 kilometers, about 6 miles up, the temperature change stopped. From that point upward, the temperature remained constant. At about 10 kilometers, something obviously changes—not gradually, but very suddenly.

- De Bort published his findings in 1902, calling the lower layer of the atmosphere the troposphere and the higher layer the stratosphere. His discovery changed the way scientists think about the atmosphere—how it moves and what it is made from. The chemistry of these 2 layers can be quite different, though equally important to the health of our environment.

THE 2 FACES OF OZONE

- Why does the temperature suddenly stop dropping as the stratosphere is reached? De Bort's countrymen, Joseph-Louis Gay-Lussac and Jacques Charles, had shown more than a century earlier that temperature should decrease with altitude as the atmosphere thinned. So, there must be an external source of energy—something pouring energy into the outer reaches of the atmosphere. And there was: the Sun.

- The Sun emits a powerful mixture of electromagnetic radiation over a broad range of wavelengths. The visible and infrared wavelengths, it would appear, traverse the atmosphere with no problem, reaching the ground and bathing us in heat and light.

- But not all that comes from the Sun is beneficial to us. In addition to the visible and infrared light, the Sun also releases a stream of ultraviolet radiation. The shorter wavelength of the ultraviolet radiation means that photons of this class of light carry more energy than their visible counterparts—enough energy to promote the breaking of bonds critical to holding our DNA together, causing cellular damage when it reaches our skin.

- Fortunately for us, the worst of this radiation, called UVC radiation, never reaches the surface. Instead, it is absorbed by a protective layer of a very special type of triatomic molecular oxygen, O_3, also known as ozone.

- Ozone had been observed in the stratosphere as early as 1913, but its critical role in protecting Earth wasn't realized until about a decade later. A British researcher named Gordon Miller Bourne Dobson, taking advantage of more precise thermometer technology, was able to show that the stratosphere temperature is not constant as de Bort had believed, but is actually slightly inverted.

- In other words, the temperature actually increases with altitude in the stratosphere. This so-called temperature inversion coupled with the discovery of high concentrations of ozone painted an unmistakable picture: Ozone was absorbing radiation from the Sun, making it slightly warmer at the top of the stratosphere, where the radiation was strongest.

- Realizing how crucial this absorption of UVC by ozone is to our plant's health, Dobson set out to create a device that could be used to monitor its concentration at specific locations. His device has come to be known as a Dobson meter. It works by measuring not UVC radiation, but rather UVB and UVA radiation. Ozone does not absorb UVA radiation at all, but it does partially absorb UVB.

- Dobson's invention makes use of Beer's law, which relates the intensity of a compound's absorption at a given wavelength to its concentration in a sample. Using the UVA intensity as an internal standard, the Dobson meter measures the intensity of UVB radiation and compares it to that standard. As the ozone level drops, the intensity of UVB radiation relative to UVA radiation increases in accordance with Beer's law.

- Using Dobson's invention, atmospheric scientists could detect thinning ozone before it became so depleted that UVC started to penetrate, making the problem life threatening.

- It is a good thing, because in 1984, a group of 3 British scientists—Joseph Farman, Brian Gardiner, and Jonathan Shanklin—made a very startling and unsettling discovery. In exploring the atmosphere above Antarctica, they discovered that a region of the ozone layer nearly the size of Antarctica had thinned substantially, bathing the continent in high-energy UVC and UVB radiation.

- Years of mapping this thin layer had revealed that each year it seemed to grow larger and larger. A class of compounds called chlorofluorocarbons (CFCs) was to blame. Chlorofluorocarbons are a class of chemical compounds invented by Thomas Midgley Jr. in 1930 during his quest to find a safe refrigerant.

- Stable and unreactive under surface conditions, when the carbon-chlorine bonds of CFCs reach the troposphere and are exposed to ultraviolet light, they break with devastating consequences. The carbon-chlorine bond releases a chlorine atom, which has only 7 valence electrons and is very reactive. Put in the presence of ozone, this chlorine atom will very rapidly steal an oxygen atom to form chlorine monoxide and a molecule of oxygen.

- Chlorine monoxide can go on to react with atomic oxygen, another species that is prevalent in the upper atmosphere. In doing so, it creates another molecule of oxygen gas (O^2) and regenerates the chlorine atom, which can go on to catalyze the decomposition of many hundreds or even thousands of ozone molecules before it's finally consumed in a scavenging process.

- We have to be extraordinary careful about releasing CFCs into the environment, because very small amounts can do a great deal of damage. The bad news is that over the 50 or 60 years that humanity dispensed these chemicals into the atmosphere with abandon, we were unwittingly destroying a critical protective layer of our atmosphere.

- The good news, however, is that we realized our mistake in time, and as use of these compounds has decreased, the ozone layer's natural equilibrium has started to reestablish itself. After the calamitous growth through the 1980s, the hole has maintained a nearly constant size since. The world waits to see if the hole will naturally begin to heal itself as the CFCs are slowly purged from the upper atmosphere.

- As beneficial as ozone is to humanity in the stratosphere, it can be every bit as dangerous to us down in the troposphere. And while we were busy destroying it in the stratosphere for most of the 1900s, we were also busy creating it where we live.

- We largely have our own voracious appetite for fossil fuel energy to blame for the phenomenon of what is known as photochemical smog. Smog—a combination of the terms "smoke" and "fog"—was first described in the 1950s. At first a curiosity, it rapidly became a plague to low-lying areas with significantly higher terrain surrounding them, such as Los Angeles, California.

- As automobile production in the United States grew, so did automobile emissions, as well as a problem that no one even realized existed at first: ozone. As helpful as ozone is in the stratosphere, it is bad news in our lungs. Ozone is not very water soluble, so it penetrates deep within the lungs. There, in the natural fluid present in the lungs, it finally dissolves and reacts with a number of biologically relevant compounds.

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Fleming, *Inventing Atmospheric Science*.

QUESTIONS

1 Acid rain can be particularly damaging to plant life because most root systems pump hydrogen ions into the soil to balance charge as they bring in vital nutrient ions, such as sodium and potassium. How does Le Chatelier's principle explain the complications that acid rain can cause for this process?

2 The well-known upper atmosphere's jet stream drives many weather patterns in the Northern Hemisphere. What are some of the chemical and physical processes involved in driving this powerful wind current?

Chemistry, Life, and the Cosmos

LECTURE 60

As we understand it, life requires a few specific conditions to evolve and thrive: the presence of water and organic molecules. Detecting these substances in deep space might seem challenging, but the techniques used to search for them are some of the oldest and most well-developed techniques known to chemists. We only need to find ways to apply them when the object under study is millions of miles or even light-years away—a pretty significant wrinkle, but not insurmountable. This search can exploit many phenomena that you have learned about through your investigation of chemistry on Earth in this course.

THE SEARCH FOR WATER

- We have always known that water is essential to life, but in recent years, as the complexity of life's biochemistry has come to light, the importance of water has really started to sink in to the human perception.

- Water is such a simple molecule. Two of the most abundant, and simple, elements in all the universe. But put them together in the right way, and you have a compound that, as far as we know, is indispensable to life.

- Our search for life, and environments that can sustain it, starts with water. But how will we look for water out there? How do we detect water on the Moon, on other planets, or even in deep space? We do it in very much the same way that we would on Earth.

- That became a real possibility with the achievement of the Apollo missions. Manned missions to the Moon gave researchers a very real chance to place instrumentation directly on the surface to look for signs of this critical substance.

- The astronauts who participated in the final few Apollo missions to the Moon placed an array of instrumentation on the surface to investigate exactly what the Moon was made of, sending invaluable information about the chemistry of our nearest cosmological neighbor. Among those instruments was a mass spectrometer, not all that different from those developed by J. J. Thomson. But years of attempts to find water with the mass spectrometer were fruitless.

- It turns out that there is a way to prospect for water without having to send a manned mission. The vibration of chemical bonds gives them the ability to absorb infrared light, but only very specific frequencies that depend on the types of atoms involved in that bond. Water does this with great efficiency—so much so that it is a property that we can look for in the atmospheres of planets simply by assessing how well they absorb certain infrared light.

- The Spitzer space telescope, now in its second decade of service, has been used to survey so-called exoplanets, or planets outside of our solar system, for traces of atmospheric gases like water, which might point to planets capable of supporting human life or harboring life all their own.

- The first thing that we look for to weigh the odds of water existing in a distant region of space is an absorption band at 3 micrometers, which falls in the infrared region of the spectrum, hiding from human eyes but detectable by the electronics in the Spitzer instrumentation. When light of this frequency is absorbed, it is usually by an O-H bond, and a sample of water is simply a huge collection of O-H bonds.

THE SEARCH FOR BIOMOLECULES

- There is still a great deal of debate over just how life got started on Earth, but we can say a few things with relative certainty. For example, there must have been liquid oceans, which means that not only was water present, but the surface temperatures of the planet were moderate enough to maintain liquid bodies of that water.

- Another must-have to produce the incredible chemical reaction that is life is carbon-based compounds. And this is where things get tricky. In a living organism, biomolecules like DNA must be self-replicating, meaning that one strand can create another.

- But there is a circular process going on in living systems. DNA is translated into RNA, which is used in the production of proteins. But those proteins assist in DNA management by performing tasks like repairing mutations and helping DNA wind up properly.

- So, you can't make proteins without RNA, and you can't make RNA without DNA, and you can't make copies of DNA without proteins. It is a classic chicken-and-egg conundrum. Which came first?

- We simply don't know. But there are some related questions that we can ask. For example, if amino acids and proteins were the original biomolecule, how could they form without the aid of a living system?

- This question was put to the test by Stanley Miller in 1953, when he created a simulated early Earth atmosphere in his laboratory and was able to produce amino acids inside of it using only nonbiological materials: water, methane, ammonia, and nitrogen.

- But Miller's experiment isn't the only possible explanation of how life began on Earth. There are other people who believe that it did not begin in an electrical storm on Earth 4 billion years ago, but rather that the materials necessary to spark life might have fallen from deep space.

- In 1969, a meteorite smashed into Victoria, Australia. Because it was observed by many, there was no arguing that this rock fell from space. A recovery effort collected more than 100 kilograms of material from the meteorite, with some pieces as large as 1 kilogram.

- What is remarkable about the Murchison meteorite is not that it hit the Earth, but what it brought along for the ride. Researchers at NASA's Ames Research Center tested freshly broken pieces of the meteorite, looking for any signs of molecules that might provide a seed for life.

- By extracting the contents of a newly exposed surface of the meteorite and then isolating the organic components using a separation technique known as chromatography, the researchers determined that there were no fewer than 7 different amino acid compounds trapped within the matrix of the Murchison.

- Over the past few decades, as analytical technology has continued to improve, the meteorite was occasionally revisited and reanalyzed. As of 2016, more than 50,000 distinct carbon-based chemical compounds have been identified within—including not only amino acids, but also purine and pyrimidine bases that are essential to the construction of DNA.

- But tests conducted on these compounds indicated that they were not likely created by a living system. This is a bit disappointing, because a different result might have proven the existence of extraterrestrial life. But if these compounds can form in lifeless rocks in deep space, and if they can fall to terrestrial planets and seed them with the materials needed for life, then it could happen just about anywhere in the cosmos.

- This idea was actually offered much earlier than the Murchison impact. In 1908, Svante Arrhenius postulated that the materials needed for life might fall from the stars in a process that he called panspermia. A process like this might explain how life was able to gain a foothold so quickly on the surface of the early Earth, and the Murchison meteorite would seem to lend some gravity to this theory.

- But this opens up an even more challenging question: If the Murchison carried with it a library of tens of thousands of different organic molecules and those molecules strongly appear to be nonbiological in origin, then how did they get there?

- How can organic compounds like amino acids and purine or pyrimidine bases form in deep space? It seems somehow impossible that atoms and simple molecules could collide in the vacuum of deep space to create something more complex.

- The answer turns out to be ice. The most promising theory involves interstellar grains of ice acting as miniscule chemical-reaction vessels.

- We have the Spitzer telescope to thank for this theory. When the telescope stares into deep space, measuring faint infrared radiation that permeates our universe, occasionally clouds of interstellar material drift into the telescope's field of view. When this happens, a fairly strong infrared absorbance is measured at about 3-micrometer wavelengths. This corresponds to the vibration of O-H bonds in ice—in deep space.

- The rest of the spectra of these features showed evidence of small molecules like carbon monoxide and carbon dioxide, as well as methanol and methane. There is even evidence of larger hydrocarbon compounds called polyaromatic hydrocarbons.

- And there are still many infrared absorbances from deep space that are yet to be identified, but very likely result from additional organic compounds trapped within those small grains of interstellar ice.

- How do we explain this spectral confirmation of interstellar ice and organics? The leading theory is that small grains of ice contain even smaller pores within them, giving them a very large surface area for their size. Because of this large surface area, interstellar atoms, small molecules, and polyaromatic hydrocarbons are preferentially adbsorbed to that surface with one another.

- So, the ice grains act like an interstellar sponge, sopping up interstellar atoms as they are encountered. This process concentrates all of these compounds in contact with the ice, allowing them all to react with one another. Add a bit of energy from radiation and you have everything you need to run a sand-grain-sized chemistry lab in deep space. From here, it isn't much of a stretch to imagine some of these grains finding their way into a forming solar system, seeding it with the compounds needed to create the spark of life.

TERRAFORMING

- In addition to understanding how life comes to be on planets, another driver for space exploration is the desire to find new outposts for human colonization. But as Venus and Mars teach us, creating the perfect balance of tectonics, atmospheric composition, and a temperature conducive to the presence of liquid water can be a tricky balancing act.

- With billions upon billions of terrestrial planets likely in our galaxy alone, it is highly probable that there are some that meet all of the necessary criteria. But there is something we can do to hedge these bets. In theory, we can improve the inhabitability of planets that show promise but aren't quite perfect through a process called terraforming, which involves changing a planet's atmospheric chemistry.

- Mars and Venus could not be any more different when it comes to their atmospheres. Venus is a crushing, acidic, runaway greenhouse, and Mars has a cold, thin, all-but-stripped-away atmosphere. In both cases, it seems that the key to bringing their environments under control is to manage the greenhouse gas content of their atmospheres.

- One suggestion involves the use of refrigerants. Fluorinated hydrocarbon gases, which have replaced ozone-depleting CFCs in many refrigeration units on Earth, might act as a jump starter for global warming on Mars. These compounds absorb infrared radiation in spades. The highly polar carbon-fluorine bonds are practically custom-made to absorb infrared radiation emitted from the surface of the planet.

- As these gases promote heating of the planet's atmosphere, more and more carbon dioxide should sublime from the poles, eventually taking over and dominating the chemistry of the Martian atmosphere.

- Even more recent advances in bioengineering are again changing the way we think about our ability to alter climates. Cyanobacteria played a large role in altering the atmosphere of our Earth. They are remarkably resilient bacteria, requiring little more than liquid water, light, and time to thrive in all but the otherwise harshest of environments. And as researchers determine new ways to make them even more robust, it seems that someday we might deliberately seed the Red Planet with cyanobacteria.

- This would be done in the hopes that they will again do for Mars what they did for Earth, consuming a portion of the newly liberated carbon dioxide in photosynthesis to create a steady source of not just any atmosphere, but one with oxygen contained therein.

- In a stunning development, NASA announced in October 2015 that its Mars rover had photographed what appeared to be a briny solution creeping down the walls of several craters on Mars. Infrared studies confirmed that the areas around these streaky formations contain high levels of hydrated minerals, meaning that water is somehow associated with their formation. If this is true, there may be life. And if that is true, terraforming Mars may be much easier than we ever thought.

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Lemonick, *Echo of the Big Bang*.

QUESTIONS

1. Do you think that we will discover life elsewhere in the universe in your lifetime? What evidence can you marshal to support your opinion?

2. What was the most useful or interesting thing you learned about chemistry in this course?

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