CHEM ATLAS

Comprising Handy Extra Materials All The Lectures As Summaries

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Contents

What is This?

The purpose of this document is to serve as a guide and resource that gives you a quick overview of each lecture. For each lecture, there is a summary of the main topics covered, the Why This Matters moment, and the new Why This Employs section, plus a few example problems. These handouts will be given by "Unit," which is the content that goes into each exam. There's also a Concept Map at the beginning of each Unit, to show how the various materials are connected together.

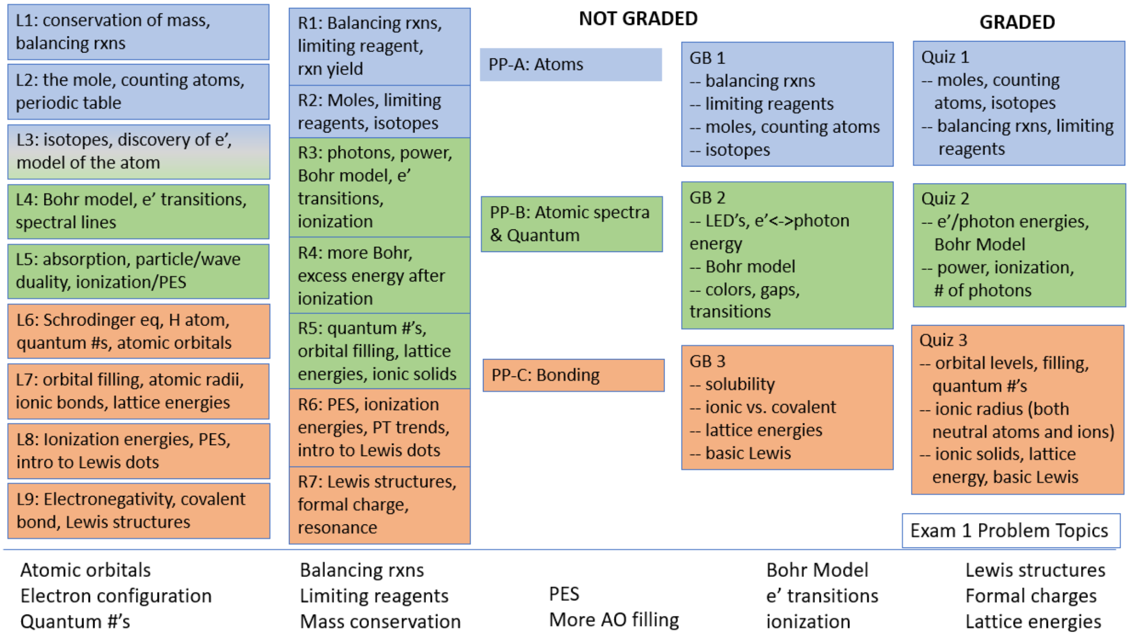
So why did we make this? We hope it's useful to get a good snapshot of any given lecture. Whether you couldn't make it to a lecture or you couldn't stop thinking about a lecture, this is a way to quickly get a sense of the content. It also gives me a chance to provide additional details that I may not have time for in the Why This Matters example, and also it lets me try out the Why This Employs section, which I certainly will not have time to discuss much in the lecture. Hopefully you find it useful, and as with anything else in this class, any and all feedback is most welcome!

One point about these lecture summaries. Please note that the lecture summaries are not meant to be a substitute for lecture notes. If you were to only read these summaries and not go to lecture, yes you'd get a good sense of the lecture from a very high level view, but no, you wouldn't get enough out of it for it to be your only resource to learn the material!

How This Connects: Unit 1, Lectures 1-9

In this class we have 36 lectures, 20 recitations, 9 goodie bags, and 12 problem sets, all tightly integrated and each one designed to contribute to your overall 3.091 learning experience. These different resources come together in the Celebrations of Learnings throughout the semester, including 9 quizzes, 3 midterms, and a final exam. For each unit, defined as the content that goes into a midterm, we have created a Concept Map to elucidate connections between the different class components so that you can see clearly the context of each.

Below is an image of the Exam 1 Concept Map. This demonstrates how each of the aspects of the course fit together: you have lots of resources! The Practice Problems, Recitations, Goodie Bags, and Lectures are ungraded resources to help you prepare for the quizzes and exams. All of the material listed on this concept map is fair game for Exam 1.



NOT GRADED

L1: conservation of mass, balancing rxns

L2: the mole, counting atoms, periodic table

L3: isotopes, discovery of e', model of the atom

L4: Bohr model, e' transitions, spectral lines

L5: absorption, particle/wave duality, ionization/PES

L6: Schrodinger eq, H atom, quantum #s, atomic orbitals

L7: orbital filling, atomic radii, ionic bonds, lattice energies

L8: Ionization energies, PES, intro to Lewis dots

L9: Electronegativity, covalent bond, Lewis structures

R1: Balancing rxns, limiting reagent, rxn yield

R2: Moles, limiting reagents, isotopes

R3: photons, power, Bohr model, e' transitions, ionization

R4: more Bohr, excess energy after ionization

R5: quantum #'s, orbital filling, lattice energies, ionic solids

R6: PES, ionization energies, PT trends, intro to Lewis dots

R7: Lewis structures, formal charge, resonance

PP-A: Atoms

PP-B: Atomic spectra & Quantum

PP-C: Bonding

GB 1
-- balancing rxns
-- limiting reagents
-- moles, counting atoms
-- isotopes

GB 2
-- LED's, e'<->photon energy
-- Bohr model
-- colors, gaps, transitions

GB 3
-- solubility
-- ionic vs. covalent
-- lattice energies
-- basic Lewis

GRADED

Quiz 1
-- moles, counting atoms, isotopes
-- balancing rxns, limiting reagents

Quiz 2
-- e'/photon energies, Bohr Model
-- power, ionization, # of photons

Quiz 3
-- orbital levels, filling, quantum #'s
-- ionic radius (both neutral atoms and ions)
-- ionic solids, lattice energy, basic Lewis

Exam 1 Problem Topics

Atomic orbitals
Electron configuration
Quantum #'s

Balancing rxns
Limiting reagents
Mass conservation

PES
More AO filling

Bohr Model
e' transitions
ionization

Lewis structures
Formal charges
Lattice energies

Lecture 1: Introduction and the chemistry of the periodic table

Summary

“Never trust an atom, they make everything up,” is a classic chemistry joke that also happens to be so true, but if we want to know which elements comprise our materials of interest, then we need to know how these elements interact with one another, how they are structured, and how the material was processed to achieve this structure. To truly answer these questions, investigators in the last few centuries have made use of the **scientific method**. This involves asking questions, gathering and examining evidence, identifying explanations, and re-testing.

One of the most exciting questions in the history of chemistry was that of the **atom**—Democritus and Leucippus hypothesized indivisible building blocks of the universe (though now we know that atoms can be broken down into even smaller “subatomic particles”). Robert Boyle, in his quest to identify different atoms, studied metal ores (naturally occurring rocks containing metal impurities) and succeeded in separating a large number of elements, including many metals. As the list of discovered atoms grew, scientists also began studying their categorization. For example, Antoine Lavoisier named four property-based categories for the 33 elements he identified: Gases, Non-Metals, Metals, and Earths. John Dalton identified 36 different elements, and designed a graphical symbol to represent each of them.

In this lecture we introduced the concept of **chemical reaction balancing**, which involves adding coefficients to the reactants and/or products in the reaction to ensure that there are equal numbers of each type of atom on the left- and right-hand sides of the arrow. This is necessary because of the **law of conservation of mass**, which states that nothing is created or destroyed at the atomic level, so the mass of the reactants equals the mass of the products. Rather, atoms can be rearranged to form different molecules. The first chemical reaction we balanced was a **combustion reaction**, which is a reaction in which a carbonaceous material burns in the presence of oxygen. We found the **limiting reagent** for this reaction, which is the reacting species (atom or molecule) that is used up first. The **yield** of the reaction is the amount of product formed.

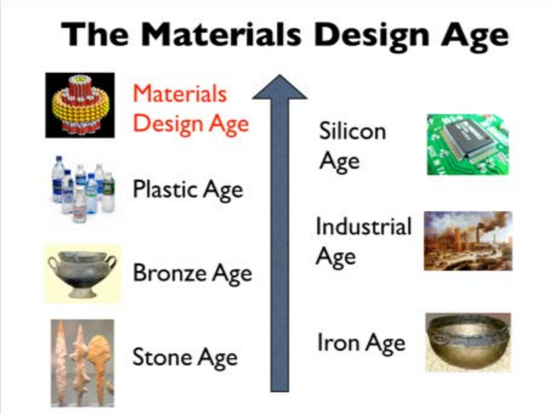
Dalton stated that atoms of a given element have a particular weight and other distinguishing characteristics. He proposed the law of multiple proportions, which says that when two elements react to form a series of compounds, the ratios of masses of the 2nd element per gram to the 1st can be expressed as ratios of integers.

Why this matters

In this first lecture, we started talking about the discovery of the elements. Well, I don’t mean to give anything away, but there aren’t going to be all that many of them in the end. In fact, to date we’ve got 118 on the official roster, but if we consider which ones we can use to make stuff for humans that number is lower, more like 80 or 90. How many elements do you think there are in your cell phone? It depends on the phone, but in mine there are 64 different elements!

That's more than two thirds of all of the ones we could even have used and it's incredible to think about. Because of this massive design potential, the world we live in has completely changed.

As a Materials Scientist, I love that we have this tradition (shout out to Danish scholar Christian J. Thomsen) of naming the age we live in by the material that mattered most during that age. But as a Materials Scientist, I also love that we'll never be able to do that again. The reason is that we truly live in a new era, one where we can realize the dream of Richard Feynman, who in his famous speech "There's Plenty of Room at the Bottom" put forth the vision for atomic-scale design and nanotechnology 30 years ahead of its time. Today, we routinely control both the choice of elements as well as their structure as they come together to make materials do things we never thought possible even just 10 years ago! In other words, we control their chemistry at the atomic scale.



Images of stone arrows, bronze pot, industrial age, plastic bottles, silicon chip © sources unknown. This content is excluded from our Creative Commons license. For information, see https://ocw.mit.edu/fairuse. Image of atomic design is in the public domain.

This gets to why this is so cool (and, you guessed it, why it matters). You see, so many of our current global challenges – whether in energy, health, or the environment – have a bottleneck that occurs because of the material that makes up a central part of the technology (in some devices it's called the "active layer"). That means that by "simply" choosing or making a different material, one has the potential to completely change the properties, cost, and manufacturability of the technology. This is unlike a previous revolution around silicon where we went from a cost of $1 per transistor in 1965 to $0.00000001 per transistor in 2015. Talk about a learning curve! That was primarily due to advances in processing of the same element, silicon, to get to smaller and smaller components. More than a billion transistors now fit nicely on a single chip. Unlike this dramatic age of silicon, many of the next technology revolutions will rely on changing the material itself: in some cases, completely. We now live in the Materials Design Age, which has come just in time since it converges with very pressing challenges on a global scale that will rely on new materials to be solved. And this is why the discovery of these elements matters so much. They are our playground and the basis from which we will make the next set of technologies to change the world for the better.

Why this employs

In this section, we'll discuss how the material in each lecture connects to real jobs. I'm trying it out this year for the first time, and since I likely won't have time to spend on it in lecture, this document is the only place you'll find it. In Why This Matters, I passionately believe that each lecture can and should be connected to some larger-scale challenge, or innovation, or inspiration. In Why This Employs, my goal is to connect each lecture with a possible field of employment. Similar to Why This Matters, this is not meant to be exhaustive but rather illustrative, to give you another way in which the material you're learning has value beyond the classroom and connects to something, in this case a job.

We spent half of this first lecture talking about the class structure, not just administratively (what's graded, what's not, etc) but also pedagogically (the different components, how they come together to provide a learning experience, etc.). Thinking about how to teach better, and how students learn, and how new technologies should or should not be a part of this, is a wonderfully rich area of employment. If you're interested in learning more, check out MIT's Teaching and Learning Lab or some of the cool initiatives in education like EdX, NEET, or the "superUROP" programs.

Another employment direction related to this lecture is the discovery of new elements. Here, we examined how the earliest chemists attempted to identify elements. This came down to smashing, burning, boiling, reacting, etc. It turns out that's still a thing, only in modern times all this reacting occurs with much bigger pieces of equipment and much larger teams of people. The next element yet to be discovered (at the time of writing, that would mean the 119th known element) will likely not have a very long lifetime, and will be very difficult to make in large quantities. But pushing the boundaries between what we have found naturally and what we can make synthetically as it relates to the fundamental building blocks of the universe... well, that's a pretty exciting thing to do. And given the prediction by some that an "island of stability" exists for heavier elements that have yet to be made, it's possible that an entirely new era of chemistry awaits such discoveries.

The last example I'll give for employment relates to the idea of the metal ores that I mentioned earlier in this lecture. Remember that this is where Dalton and many others were discovering those new elements. Basically, you take a rock and carefully break it up and viola, you get Fe out of it (ok, it's a bit more complicated than that, but that's the idea). It turns out that quite often the metal atom is locked up pretty tightly in the form of an "oxide" (yes, that means bonded to oxygen, but we'll get to that in a few lectures). The point is that extracting metals like aluminum from rocks takes an enormous amount of energy, which means it requires a lot of burning of fossil fuels. What if you could come up with a new, much "greener" way to get metals or minerals in their pure form out of the rocks from which they originate? This would be a very big deal. Mining metals and minerals involves massive teams of engineers who cover a wide array of jobs from figuring out where to mine, to characterization of the starting materials, to optimizing extraction chemistry, to working on new ways to do that more efficiently.

Example Problems

1. In this lecture, you witnessed my passion for pyrotechnics.

a) Write and balance the chemical reaction for a similar process, the combustion of propane (C_3H_8).

b) If you have 500g of propane, how many moles do you have? How many molecules?

Solutions

1. a)

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

b) First, find the molar mass of propane.

$$3 * 12g/mol + 8 * 1g/mol = 44g/mol$$

Use the grams given and the molar mass to convert to moles:

$$500/44 = 11.36mol$$

Lecture 2: Counting Atoms and Organizing the Elements

Summary

This chapter, we introduced the concept of the **mole**. This is a constant number, also referred to as **Avogadro's number**, equal to 6.0221409×10^{23}. The **atomic mass units** (AMUs) assigned to an element are equal to the mass in grams of a mole of atoms of that element. Just as Avogadro's number is just a number, the AMU is just a mass, and 1 AMU is equal to 1.67377×10^{-24} grams. Just like the mole, an AMU is another special unit that chemists use to connect the very small world of atoms with the comparatively large world of things we work with. This link between the macro and atomic worlds means that by simply measuring the mass of a substance, we can know how many atoms of that material we have.

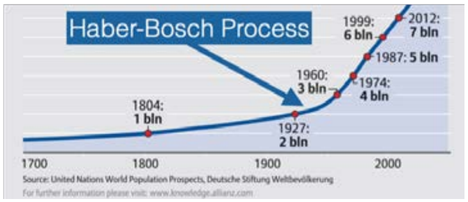
In class we used the example of the combustion of a candle, otherwise known as the nicely balanced reaction $C_{25}H_{52} + 38O_2 \rightarrow 25CO_2 + 26H_2O$. We used this example to emphasize how the concept of the mole gives us a link between the atomic and macroscopic worlds, between grams and atoms. We also used this example to re-emphasize the concepts of limiting reagent and yield.

Next, we focused on organizing the periodic table. Unlike in the last chapter, here organization means more than coming up with a naming scheme or a simple categorization of the elements, as Dalton, Lavoisier, and many others had already done. In this lecture what we mean by organization is really pattern recognition. Scientists were starting to see patterns emerging among the elements, and the more elements were discovered, the more effort was put to understanding these patterns.

Dmitri Mendeleev developed the precursor to today's periodic table. His big breakthrough was that he arranged the then-known (63) elements not just by their mass, but also by the repeating (periodic!) patterns he observed in their properties. This led him to leave gaps in the periodic table that would later be filled with newly discovered elements. Because of the periodicity in properties, he could even predict the properties of many as-of-yet undiscovered elements. The rows of your periodic table are called periods, and the columns are called **groups**. The **Main Group Elements** are those in periods two and three. There is a general trend from metallic to non-metallic elements along the periods. The **Transition Elements** are in groups 3-12 and periods 4 and 5.

Why this matters

The population of humans on this planet has seen a dramatic, exponential growth. Let's zoom in on where the growth really started to kick into high gear. See that uptick, around the early 1900's? Notice the massive change in slope. That's when we figured out how to make nitrogen in a way that plants can use.



In other words, with the discovery that is now known as the Haber-Bosch process (named after the German chemists Fritz Haber and Carl Bosch), the world was able to make fertilizer in the abundance needed to feed billions. The key comes down to something called “fixing” nitrogen. Plants need nitrogen to grow, but most plants cannot use any of that plentiful 78% N_2 that’s in the air. Instead, they need it in a form that serves up single N atoms, like ammonia (NH_3). SO how can we go from N_2 to NH_3? Easily, with the following chemical reaction:

$$N_2 + H_2 \rightarrow NH_3$$

Ah, sorry, let’s balance that:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

That’s better. What Haber and Bosch actually did was develop a catalyst and process that allowed this reaction to be carried out much more efficiently than previously. But catalysis is getting a little ahead of ourselves. For now, let’s focus on the balanced reaction and count some atoms.

In 2019, 500 million tons of nitrogen is produced for fertilizer each year using the Haber-Bosch process. Half of the protein in all human beings on this planet comes from nitrogen that was fixed by this process! So here’s my question: how long can we continue fixing nitrogen this way? And since the reaction tells us we need both N_2 and H_2, which one would be the limiting reagent?

From all of our discussion so far in this lecture we know that we can use the periodic table to determine that 1 mole of NH_3 is 17 grams. Just for simplicity, suppose in the future we continue needing to make the same amount we’re making today, namely 500 million tons of NH_3 per year. There are roughly a million grams per ton, so 500 million tons per year 500 × 106 × 106 grams per year. Dividing by 17 grams per mole, this means we need to make roughly 30×10^{12} moles of NH_3/year. Given the balanced reaction above, this means we’ll need as input to the reaction 15×10^{12} moles of N_2 per year. Now, the mass of the atmosphere is about $5.15 * 10^{21}$ grams, of which 78% is N_2, so that makes about 4×10^{21} grams of N_2 in the air. And since the atomic mass for a nitrogen atom is 7, then it’s 14 for N_2 which means there are 14 grams per mole of N_2. So the number of moles available in the atmosphere is 4×10^{21} grams of N_2 / 14 grams/mole $= 3.5 \times 10^{20}$ moles of N_2 in the atmosphere. Well that’s good news! Taking 3.5×10^{20} moles of N_2 total and dividing that by 15×10^{12} moles of N_2 needed per year, we find that we could keep at it with the Haber-Bosch process of fixing nitrogen from the atmosphere for more than 20 million years or so before using it all up.

That’s just cool. Think about this: we just went from atom to macroscopic world and it’s all because we have this concept of the mole. But we never really answered the question, namely which one is the limiting reagent in the reaction, the N_2 or the H_2? We now know how long N_2 will last us if we were to use it all up in this reaction, so what’s left is to do the same thing for H_2. Speaking of which, where will we even get H_2? Certainly not from the air. I’ll let you all work through this but here’s a hint: the oceans contain a whole lot of water, like more than 10^{18} tons. Maybe you don’t even need to do any calculations to figure this out!

Why this employs

How does counting or organizing atoms lead to a job? Well, for one thing we're talking about order, precision, and measurement. After all, Mendeleev's success relied on combining careful measurement of properties with precise ordering. This skill is needed for many different jobs. One place with measurement as its mission is the National Institute of Standards and Technology (NIST). Check out the tag line in their Materials Measurement Laboratory: "MML serves as the national reference laboratory for measurements in the chemical, biological and material sciences. Activities range from fundamental and applied research to the development and dissemination of certified reference materials and data to assure the quality of measurement results." And that's just one of their many divisions.

Another job that comes to mind is one related to the fertilizer discussed in our Why This Matters. The three fundamental constituents of commercial fertilizers used throughout the world are nitrogen, phosphorus, and potassium. As we know, nitrogen requires fixing. Potassium must be obtained in other ways. For example, it comes nicely with chlorine as potassium chloride (KCl), but we'd prefer not to have chlorine in the soil since it can lead to toxicity in the crops and high acidity and salinity in the soil. However, getting potassium in other forms is expensive and requires, as you might guess, chemistry. To make matters more complicated, both the natural sources for potassium and the specific soil needs are highly dependent on geography. For farmers in tropical regions in Brazil and some countries in Africa, the soil and rock compositions require fertilizers that better match the chemical needs of plants than are currently available. As a solution, more fertilizer is added to achieve as much crop yield as counterparts in the north, but many of the basic ingredients, especially the potassium, are produced in more northern regions and therefore are much more expensive in the Southern Hemisphere. The need for local, sustainable fertilizing solutions to increase yields is urgent! But this is starting to sound more like a second edition of Why This Matters and less like a Why This Employs. My point is that the development of fertilizers is a problem of chemistry, and the world is in desperate need of new solutions. In terms of jobs, this could mean becoming something called an "Analytical Chemist" which means you apply the principles of chemistry to figure out what stuff is made of, what the precise compositions are, how to monitor it, modify it, etc. This could also mean working at a company or research lab that develops cutting edge ideas (like recent work on using electrochemistry to make potassium).

Extra practice

1. Solar cells sometimes contain a titanium (Ti) coating that stops the cell from short-circuiting. The Kroll Process for making titanium metal out of titanium oxide is:

$$TiCl_4 + Mg \rightarrow MgCl_2 + Ti$$

a) Balance the reaction.

b) If you have 50g of both TiCl4 and Mg, what is the limiting reagent in the reaction?

c) What is the yield of the reaction in grams?

d) Plot the yield of Ti (g) as a function of increasing Mg available for reaction.

Solutions

1. a)

$$TiCl4 + 2Mg- > 2MgCl2 + Ti$$

b) Molar mass of Mg: 24.3 g/mol
Molar mass of $TiCl_4$: 189.9 g/mol

Find the moles of each reactant by dividing 50g by the individual molar masses:

$$50g/24.3 = 2\,mol\,Mg \qquad\qquad 50g/189.9 = 0.3\,mol\,TiCl_4$$

Use the mole ratio from the balanced reaction (1 mol $TiCl_4$/2 mol Mg) to see how much TiCl4 could be used up with the amount of Mg you have available:

$$(2mol\,Mg\,available)/(2mol\,Mg/1\,mol\,TiCl_4) = 1\,mol\,TiCl_4$$

1 mol $TiCl_4$ would be used up if we had an endless supply of it with the amount of Mg we have. This amount of $TiCl_4$ is more than the amount we actually have available, meaning that the $TiCl_4$ will run out before the Mg. $TiCl_4$ is therefore the limiting reagent.

c) To calculate the Ti yield of the reaction, we use the ratio of Ti to $TiCl_4$ (because these two have a 1:1 molar ratio) and then convert from moles to grams of Ti:

0.3 moles of $TiCl_4$ are being used (it's the limiting reagent, so it will be used in its entirety) and because of the 1:1 molar ratio we know that 0.3 moles of Ti will be produced. Multiply this number by the molar mass of Ti:

$$0.3 * 47.9g/mol = 14.37g\,Ti$$

d) The plot of Ti grams (on the y axis) vs. Mg grams (on the x axis) starts at 0 and increases linearly until the Ti grams reach 14.37 g, at which point we run out of $TiCl_4$ and the reaction will stop.

Lecture 3: The Discovery of the Electron and the Structure of the Atom

Summary

This lecture began with discussion of ground-breaking experiments that brought the scientific community closer to understanding the structure of the atom. These included J.J. Thomson's experiments with the cathode ray tube (CRT), which allowed him to find the charge-to-mass ratio of **electrons**, which he realized were negatively charged particles found in all atoms. Robert Millikan was able to ascertain the mass *and* the charge of the electron using his oil drop experiment. The atom was not the most fundamental particle after all, rather it was made of smaller particles like electrons, and as we learn next those smaller things that make up atoms have a structure to them. The electronic structure.

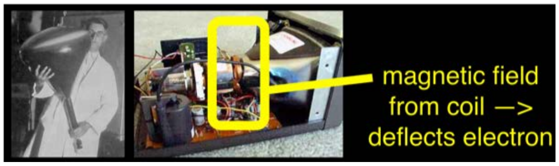
Building on the radiation studies of Marie and Pierre Curie, Ernest Rutherford was able to identify three types of particles found in radiation: **alpha particles**, which were large and positively charged, **beta particles**, which were small and negatively charged, and **gamma rays**, which didn't deflect or interact with the photographic plate in Rutherford's experiment at all. Rutherford then conducted the gold foil experiment, which showed that atoms have positive charge that is localized in the core of the atom rather than dispersed among the negative charge, as Thomson had proposed. This positively charged center of the atom is called the **nucleus**. The positively charged particles in the nucleus are called **protons**. For any neutral atom, the number of protons present must equal the number of electrons present. This number is called the element's **atomic number**, which is denoted by the letter Z. Except for the case of a neutral hydrogen atom composed of only one proton in its nucleus and one electron, all atoms also contain **neutrons** in their nuclei, which are, as the name might suggest, neutrally charged particles. To obtain the **mass number** of a given atom, the number of protons and neutrons in that specific nucleus are added together. Atoms of the same element can have different numbers of neutrons. This makes them different **isotopes** of the same element. To obtain the mass given for each element in your periodic table, a weighted average is taken of the mass numbers of that element's naturally occurring stable isotopes. The weight is assigned according to the isotopes' percent abundance in nature.

After Rutherford's experiments, there remained the question of how an atom structured in this way could be stable. Niels Bohr was the one who postulated that the angular momentum of the electrons in atoms must be quantized, which means that it takes on discrete values. This meant that the electron's energy and distance from the nucleus were quantized as well—the electron can only occupy certain orbits.

Why this matters

The discovery of the electron led to a profound new understanding of the atom, which in turn led to an entirely new theory (quantum mechanics), which in turn led to orbitals, bonding, and the building blocks for all of modern chemistry, as we'll see soon. But the discovery of the electron also led to a new capability that revolutionized the world: the ability to paint with electricity. The phosphor screen that was on the end of Thomson's cathode ray tube was the precursor to television, and the beginning of a technological revolution that changed almost every aspect of our lives. TV wasn't invented by Thomson himself, but Thomson's discovery of this new fundamental paint brush – the electron itself – was crucial for the concept to take off. Look at what the man on the left in this image is holding: it's an early version of a TV, which you can now recognize as a giant cathode ray tube! John Logie Baird was one of the first to commercialize television sets, selling his first one in 1925. You can see the inside of an early TV in the middle picture: note that it was comprised of a CRT plus a coil to induce a magnetic field – essentially the same setup that Thomson used in his groundbreaking experiments.

If electrons were scanned across the phosphor screen fast enough, an image could be painted so many times per second that it looked like motion to the human eye. This was easy to do, because changing a magnetic field quickly and precisely (to position electrons on the screen) can be achieved with simple electronic circuitry. Over the next generation, electrons became a dominant way to exchange visual information. The chemistry of the screen itself is also essential. A 'screen' is actually a phosphor coating that was often put on a piece of glass and was the target of the electron beam. Phosphor is a broad term for materials that emit light in response to a stimulus. This act of emitting light is called luminescence. It can get confusing since the term "phosphorescent" means that the material slowly emits light over time after being stimulated. A good example of a phosphorescent material would be glow-in-the-dark toys, where the stimulus is light, and the phosphor can keep glowing for many hours. On the other hand, a "fluorescent" material also emits light in response to a stimulus, but as a quick flash lasting nanoseconds. The term phosphor can refer to either of these, but the coating on the CRT screen and in those early televisions is the fluorescent kind. You can imagine why: if it didn't emit light quickly,, the image would have afterglows that lasted for hours, which wouldn't exactly make for a nice movie-watching experience.



Man with CRT & open TV images © sources unknown. This content is excluded from our Creative Commons license. For information, see https://ocw.mit.edu/fairuse.

To make matters even more confusing, the term phosphor (which as we just established can refer to materials that are phosphorescent or materials that are fluorescent), is not to be confused with the element phosphorus. Phosphorous also emits light, but of a different nature entirely, since its glow comes from a chemical reaction (a process called "chemiluminescence"). So, to sum up: the screen we're talking about uses a phosphor which is fluorescent, not phosphorescent, and doesn't have any phosphorus in it. Great.

Chemically speaking, what are these phosphors? There are so many different materials that are phosphors that it would take an entirely separate book to go through them all. They can be small molecules, complex solids, or liquids. They can emit light in response to many different stimuli, from light to heat to electric fields to the electrons we're discussing here in our CRTs. The first television screens were black and white, so the goal was simply to use phosphors that glowed white when they were struck by electrons. Powders made from zinc, cadmium, and sulfur and a dab of silver were early ingredients. In order to achieve color TV, blue, green, and red phosphors were needed. The electron beam could be pointed at whichever ones were needed to make a given color, again using the magnetic field to guide the electrons with fantastic precision. It turned out the green and blue phosphors were pretty straightforward to make, zinc-sulfide with a touch of copper for green, and silver for blue. But red was a different story: for red phosphors it took additional decades' worth of research to find anything that worked. This is the reason why color television didn't come on the scene until the mid-1960's, a full 40 years after black white television was introduced! The red phosphor challenge was finally solved by using a complex mixture of yttrium, oxygen, sulfur, and a bit of europium for good measure.

Since we've listed yttrium, I have to mention that it is one of four – yes four! – elements that were discovered in the same cave in the same town, Ytterby, Sweden. Yttrium, terbium, erbium, and ytterbium are all named after this town. We're still waiting for cambrium or bostonium.

Now, it's only your parents or grandparents who will remember what watching TV on a CRT was like. That's because TVs nowadays work on a different principle, namely light emitting diodes (LEDs). But in the end, it's still painting with electrons! An LED emits light using the cascade of electrons from high energy to low energy in a solid material. We'll learn all about that material (it's called a semiconductor) and why electrons can make light this way a little later in the semester. The light that comes out of an LED in your TV (or phone or tablet) still often passes through a phosphor, since the phosphor can be used to fine-tune the color of light we see. In this case the phosphor is stimulated by light instead of electrons, but the outcome is the same: light and color are produced using electrons and chemistry.

Why this employs

How can we get a job based on the discovery of the electron? That's kind of like asking how we can get a job related to the knowledge of atoms – in other words, electrons and atoms make up everything so anything would qualify, at least if it has any reference to matter in the employment description. But how about if we go back, specifically, to that first beam of electrons that Thompson made to discover their very existence. . . what jobs might involve beams of electrons. We already discussed painting with electrons in the topic of displays in Why This Matters, but it turns out there's a whole lot more you can do with a beam of electrons than just make pictures. To do so, though, we'll need more power. A lot of power.

If you crank up the power of that electron beam enough, and you keep it in a vacuum (just like Thompson did) to make sure they don't scatter off of anything, then you can use the electron beam to create very localized heat, enough to melt any material. If it's done to join two materials together in a precise manner we call it welding. Electrons have a lot of advantages in welding because they can be focused to very small areas using magnetic fields, and the power can be dialed in to whatever the job requires (and there's almost no limit to how powerful you can make a beam of electrons). On the higher end, for industrial welding, electron beams can get up to much as 10,000,000 Watts per mm^3 which can heat up a metal at a rate of 1,000,000,000 Kelvin per second!

Electron beam welding is a big industry, and there are many jobs associated with it. You could weld metal parts together at GE for its aviation business, and I mention that company specifically because it was James Russel who invented electron beam welding while he was at GE, back in the 1950's (as a fun side note, he also invented the first CD). If you do a search for electron beam welding you'll find huge numbers of listing for companies that provide it as a service to other companies. Bodycote, for example, states that they are, "the world's leading provider of heat treatments and specialist thermal processing services," and with 5,700 employees in 26 countries they have a lot of jobs. But there are many smaller scale operations that hire people who like to shoot massively high energy electrons at metal parts, like the family-owned Roark in Brownsburg, IN, which boasts one of the largest electron beam welding chambers in the U.S., or Precision Technologies, Inc., which has a cool-sounding 5-axis electron beam welder that goes up to 150 kV, "capable of welding parts as small as a few grams up to ones weighing several tons," or how about Fraunhofer FEP which develops customized electron beam technologies and states, "Using electrons we improve your materials and products!" Cool.

Extra practice

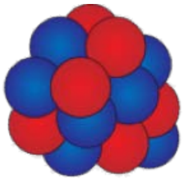
1. Your friend Wonder Woman tells you that her bracelets are made of a metal, Feminum (this is legit, it was in the '70s TV show), only found on her home island. Feminum (symbol Fm) has atomic number 120 and atomic mass 285.47. The element has 2 isotopes, ^{285}Fm and ^{X}Fm. The natural abundance of ^{285}Fm on the island is 77%.

   a. What is the other isotope, and what is its natural abundance?

   b. How many protons and neutrons does each isotope have?

2. The number above the Li symbol on the periodic table (on the right) is the number of protons in a lithium nucleus. What is the number below the symbol? How do you calculate it?

3. Assuming all the protons (red) and neutrons (blue) are visible, use proper notation to write out the atom that corresponds to each of the following nuclei:



Solutions

1. 77 % abundance of one isotope implies 23 percent abundance of the other, since we know there are only two isotopes. The atomic mass is the weighted avg. of the two isotopes. Solve the weighted average equation to obtain the missing mass number:

$$(0.77)(285) + (0.23)(x) = 285.47 \qquad\qquad x = 287.04,\ \textit{rounds to}\ 287$$

2. The number below the atomic symbol is the atomic mass. It's not specific to the atom—it's a weighted average of the element's stable (non-radioactive) isotopes, with weights given according to the isotopes' abundance in nature.

For example, lithium's atomic mass is 6.94, and its two stable isotopes are 7 (92.4% abundance) and 6 (7.6% abundance)

3. a) mass : 13, atomic : 6, atomic symbol: C

b) mass : 7, atomic : 3, atomic symbol: Li

Lecture 4: The Bohr Model and Electronic Transitions

Summary

The **Bohr model** is a framework used to describe the **quantized** nature of atoms. By assuming that electrons orbited around atomic nuclei—like planets around the sun—Bohr showed that the electrons bound to atomic nuclei can only exist in discrete energy levels. By equating the attractive force of the Coulomb interaction between the negatively charged electron and the positive nucleus, $F_{Coulomb} = -Ze^2/r^2$, and the repulsive force due to rotation, $F = mv^2/r$, and substituting the quantized angular momentum, $L = mvr = nh/2$, we find formulas for the quantized radius and the quantized energy. The energy of an electron in the nth energy level of an atom which has Z protons is

$$E = -13.6Z^2/n^2 \quad [eV]$$

The integer n, which can have any positive value ≥ 1, is called a quantum number because it makes it so that the energy can only take on certain, discrete values as opposed to a continuum of possibilities. The state n=1 is the **ground state**, and higher energy levels are called **excited states**. When an electron goes from a state with a lower quantum number to one with a higher quantum number, the energy of the electron becomes less negative: it gains energy. We know that energy must be conserved, so the energy gained in such a transition must come from somewhere. In fact, a photon with exactly the ΔE between two energy states in the atom can be **absorbed**, exciting the electron. Similarly, if the transition happens in the opposite direction, the excess ΔE can be **emitted** in the form of a photon.

The kinds of photons capable of being absorbed or emitted by a Bohr model atom or molecule can be equivalently characterized by their energy, frequency, or wavelength. Einstein taught us that light can also be quantized in his work on the photoelectric effect: the energy of the photon can take discrete values:

$$E = hf = hc/\lambda$$

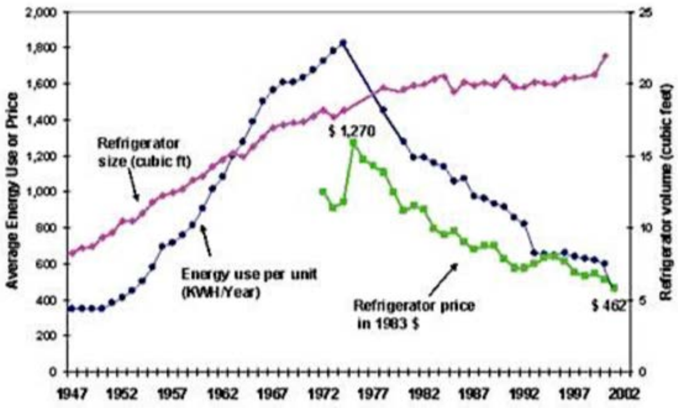
Where f is frequency, λ is wavelength, h is Planck's constant, c is the speed of light, and the second equality is true because c=fλ. The wavelength of light that can interact with a particular energy transition can be found by equating the two expressions above. With this in mind, we see that light can be used to probe what electronic transitions are happening in an atom or molecule, and therefore what energy levels are present in a material. The Bohr model fit the spectral lines of stars observed previously by astronomers; in particular, the discrete wavelengths emitted by hydrogen gas that had been observed by spectrometer finally had an explanation.

There are a few limitations to the Bohr model. We now know that electrons are not really orbiting the nucleus (although their angular momentum is quantized as predicted). Further, the Bohr model can only be used to describe electronic transitions with a single electron, such as H, He^+, or Li^{2+}. However, the key takeaways hold: if the energy states in an atom or molecule are known, the wavelengths of light that can be emitted or absorbed by the material are also determined. Likewise, if the discrete wavelengths emitted or absorbed by an atom or molecule are observed, the energy levels available to an electron are also known.

Why this matters

How does absorption of photons by electrons that are transitioning from one energy level to another matter? One application this principle is connected to is the refrigerator(!) That might not seem obvious at first, but let's see why. Take a look at the average energy used by a fridge in the U.S. over a 55-year period. It's interesting to note that the average size of a refrigerator grew steadily for 35 years and then plateaued in the 1980's.

This, it turns out, was not because people didn't want more fridge, but rather because they couldn't fit anything larger through the kitchen door. More to the point, note that the energy use per unit increased along with the size for 30 years, until suddenly it started decreasing rapidly in the 1970's, even though the size continued to increase. This is because during that time there was also an oil shortage and people were starting to get concerned about energy use. Some of these people had important titles like President of the United States (Nixon, Ford, and Carter), and a whole lot of legislation aimed at energy conservation happened because of them. For example, President Ford signed the first law ever on this topic in 1975, the Energy Policy and Conservation Act, which led to the establishment of fuel economy standards for cars and efficiency standards for appliances. After that, more laws were signed that created incentives to lower energy consumption (towards a goal of making the U.S. an energy independent nation by 1985), with Carter presenting a plan to congress stating that, "conservation is the quickest, cheapest, most practical source of energy," requiring federal agencies to develop energy conservation plans, and creating the Department of Energy (DOE).



Average energy use vs. time © source unknown.

In this Why This Matters, I want to emphasize the importance of government policy. It was the government stepping in that led to the technological innovation that led to greater efficiency and lower costs. In 1992, the Energy Star program was introduced which led to even greater reduction in the energy consumption of appliances and critically increased consumer awareness. Not only did refrigerators themselves become cheaper because of this innovation, but the energy they used continued to decrease. In 2019 in the U.S., we save about \$20 billion annually on energy consumption alone for our refrigerators compared to the 1970's. Sadly, since 2017, the Trump administration has been trying to eliminate the Energy Star program, which many consider to be one of the most successful voluntary energy efficiency programs in the world. It has saved Americans \$430 billion in energy costs across hundreds of appliances, not to mention the lower CO_2 emissions that have resulted.

Now we still haven't connected back to our chemistry lesson, and while I could do that for the energy savings alone, there's another example involving a fridge-related policy decision that very clearly brings Bohr back to the table. That is the Montreal Protocol, which was signed in 1987 and was the first treaty to be ratified by all countries in the world. It represented universal agreement to protect the stratospheric ozone layer by phasing out both production and consumption of ozone-depleting chemicals, like chlorofluorocarbons (CFCs). Taking this action led to the recovery of the earth's ozone layer that protects life from harmful UV radiation. Millions of lives have been saved as a result. But what is it about CFC's that makes them deplete ozone? And why is ozone so important for blocking UV radiation? The answer, of course, comes from chemistry.

Ozone is a molecule consisting of three oxygen atoms, O_3, and a common CFC molecule consists of a carbon atom, three chlorine atoms, and a fluorine atom, CCl_3F. Occasionally, the CFC molecule breaks down and gives up one of its Cl atoms, like this:

$$CCl_3F(g) \rightarrow CCl_2F(g) + Cl(g)$$

Note the "(g)" subscripts are included to show that all this is happening in the gas phase. Once a chlorine atom is freed up, it can then react with ozone, like this:

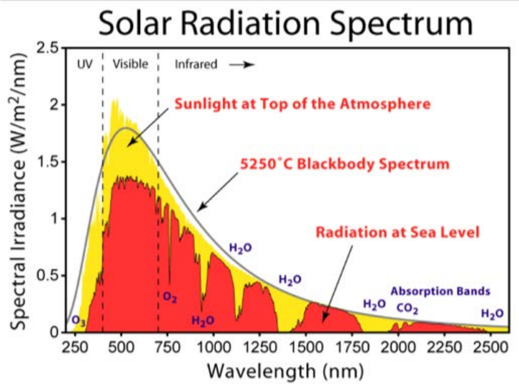
$$O_3(g) + Cl(g) \rightarrow ClO(g) + O_2(g)$$

And so each CFC molecule can deplete one ozone molecule. But it doesn't stop there. A third reaction takes place, since there are also oxygen atoms in the stratosphere. When an oxygen atom interacts with the ClO molecule, it reacts with it to make O_2, like this:

$$ClO(g) + O(g) \rightarrow Cl(g) + O_2(g)$$

And therein lies the real problem: the Cl atom is now free again and ready to attack another ozone molecule. Because of this catalytic cycle, one single CFC molecule can lead to the destruction of 100,000 ozone molecules!

That brings us to the second question from above: why does losing ozone lead to more UV radiation? This is where electron transitions come in. Check out the plot in this figure of the solar spectrum. The x-axis is the wavelength of light coming from the sun, covering only the UV, visible and infrared (so it is just a sliver of the full EM spectrum we showed a few pages back). The y-axis is the intensity of light at a given wavelength, in Watts per area. A Watt is a measure of power, which is energy per time, or Joules/s. In plain words, this is a plot showing the power of sunlight as a function of its color.



Solar radiation spectrum by Robert A. Rohde as part of the Global Warming Art project. License: CC BY-SA. Source: Wikimedia Commons.

The first thing to point out on the plot is that solid black curve, which corresponds to a theoretical prediction of the black body radiation emitted by an object at the temperature of the sun. This temperature varies a lot depending on where in the sun it's measured, but near the surface, T=5250°C is a decent approximation. Note that it's a nice continuous spectrum, and it has a shape typical of black body radiation (remember, that's the kind of radiation we mentioned earlier – the kind that Planck introduced the concept of quantization to explain).

Next, there's the yellow shaded parts that correspond to the actual measured power from the sun before it interacts with our atmosphere. It follows the black body radiation quite well, which validates the prediction. And then, there's the red shaded region. This is the power from the sun as measured on earth, so the only difference between the red and the yellow is that the red is a measurement of photons from the sun that have passed through the atmosphere. It follows the yellow pretty well in general, except that now there are gaps in the spectrum: discrete wavelengths where there is no light observed on earth at all! The plot shows the reason why: next to some of the larger gaps, there is a molecule. H_2O is listed in several spots. One gap is attributed to O_2 and another to CO_2, and one of those gaps is due to our nice, friendly, no-longer-getting-depleted ozone molecule, O_3. It's the gap all the way over on the left side of the plot, and it's right where the UV light would have been shining down on us. We can see that it does indeed shine down on us outside of the atmosphere (the yellow), but not at the earth's surface (the red).

This tiny sliver of absence of UV light due to the O_3 molecule is absolutely essential for life on earth as we know it, and it's all thanks to electrons being pumped up in energy from one state to another. In this case it happens in a molecule, not an atom, but the same principle we learned in this lecture for electron transitions according to the Bohr model applies. There are discrete energy states where electrons are allowed to be in the O_3 molecule, and transitions between these energy levels can happen when an electron either absorbs or emits a photon. Just like the Bohr model for the hydrogen atom, the discrete nature of electronic transitions in molecules means that absorption of light occurs only at distinct points in the spectrum. For ozone, there just happens to be an energy difference between two electron states that has the energy of a UV photon, which is why this particular molecule absorbs well in the UV.

Why this employs

I was thinking about mentioning jobs in spectral astronomy, since the Bohr model explained the observation of spectral lines from hydrogen and other light elements out in space. The same type of analysis, using basically just a (much) fancier version of the spectroscope you got in your Goodie Bag, is used today to understand the stuff that makes up distant stars, nebulae, galaxies, quasars, all sorts of other intergalactic matter, including whether exoplanets have earth-link atmospheric compositions.

But instead of going down that outer space route, I'd like to pick up here on the point I made in Why This Matters, regarding how solving the ozone depletion problem is a beautiful example of how important science policy can be in making the world a better place. What employment opportunities are there along such lines? "Science policy" is a broad term that can apply to a wide array of jobs and activities, from deciding how science is funded to how it can (or cannot) be translated into commercial products, to how science impacts human health to protecting the health of the environment. The jobs that result from this direction often involve a connection to politics and Washington (if in the U.S.) but they don't necessarily have to. One way to get involved is through fellowships, where students can engage with policy-makers in DC for a summer or a semester.

There are a number of options along these lines, like the AAAS Diplomacy fellow (check out https://www.aaas.org/programs/science-technology-policy-fellowships), or fellowships at the Science and Technology Policy Institute, or the White House Office of Science and Technology Policy (OSTP). And then beyond such general ones there are many specialized fellowships in science policy that go by the sub-field, like the American Geophysical Union Congressional Science Fellowship, or the various NOAA Sea Grants for ocean-related policy, or the John Bahcall Public Policy Fellowship for astronomy. And many more.

Beyond fellowships there are tons of jobs out there, like at science policy centers, think tanks or other organizations, from the Union of Concerned Scientists, to the RAND Corporation, to UNESCO, to the Federation of American Scientists, to the Center for Science in the Public Interest, to University-based centers like Arizona State's Consortium for science policy and outcomes. These are only a very few examples – there are so many more. You could get involved directly with the science funding agencies like the NSF, DOE, or NIH (if you become a program manager at any of those please give me a call). Science policy is an incredibly important part of what science is, what it can become, and how it can be used most effectively, wisely, and for the good of the world.

Extra practice

1. What is the energy associated with the ground state in a lithium ion?

2. If a light wave has the same magnitude of energy as the lithium ground state, what are the frequency and wavelength of this light?

Solutions

1.

$$E_n = -R_y \frac{Z^2}{n^2} = -13.6 \frac{3^2}{1^2} = -122.4 eV$$

2.

$$E = h\nu = \frac{hc}{\lambda}$$

$$122.4[eV] = \frac{(4.14x10^{-15}[eVs])(3x10^{8}[m/s])}{(\lambda[m])}$$

$$\lambda = 9.9 \times 10^{-7}[m]$$

Lecture 5: Wave-Particle Duality and Quantum Mechanics

Summary

This chapter, we continued our discussion of ionization. We restricted our examples to ionization of hydrogen atoms in order to use Bohr's model of the atom. An electron in the ground state, or lowest energy state, of a hydrogen atom has an energy of -13.6 eV. Therefore, this electron's ionization energy, or the energy required to free it from the nuclear pull and effectively transition it to energy level n=∞, is 13.6 eV. The ionization energy of an electron in an atom with atomic number Z can be found with the following formula:

$$\Delta E_{ionization} = -13.6Z^2 \quad \frac{1}{n_f^2} - \frac{1}{n_i^2}\Bigg)\Bigg(eV]$$

Ionization energy can be thought of in terms of Einstein's **photoelectric effect**. In his groundbreaking experiment, Einstein shone light (streams of photons) of different energies onto slabs of metal. The photons had to reach a minimum threshold energy in order to ionize the metal atoms. It makes sense that metals with higher first ionization energies will be better able to hold on to their electrons. In other words, light with higher frequency will be necessary to ionize metals with higher first ionization energies. **Photo-Electron Spectroscopy (PES)** is a characterization technique that involves ionizing materials with photons and measuring the removed electrons' kinetic energies. The energy of the bound state of each removed electron can be calculated by finding the difference between the incoming photon's energy and the resulting kinetic energy of the freed electron.

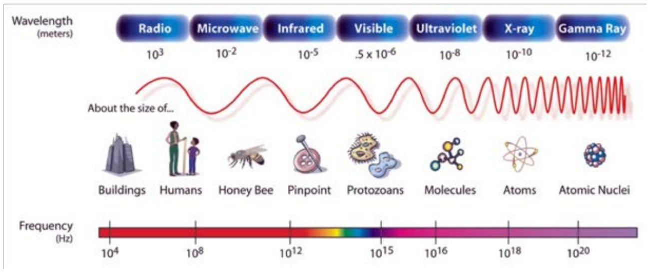
The Bohr model couldn't explain quantization of electron levels; they were imposed in the model, but not understood. Through a series of experiments in the early 20th century, **wave-particle duality** was demonstrated. This meant that light waves were shown to behave as particles, and particles were shown to behave as waves. The most famous of these experiments was the double-slit experiment, where electrons were shown to act like both waves and particles. Louis de Broglie showed that *all* matter acts like a wave and has a corresponding wavelength (λ). This wavelength can be found using the de Broglie relation, where p is the object's momentum, which is equal to its mass times its velocity, and h is Planck's constant:

$$\lambda = \frac{h}{p}$$

Erwin Schrödinger, with **The Schrödinger Equation**, described the relation between a wavelike particle's spatial distribution and its allowed energies. In the Schrödinger equation, quantization is a natural consequence of solving for a standing wave. This wavefunction ψ does not have direct physical meaning, at least that we know of, but its square $|\psi|^2$ corresponds to the probability of finding the particle at any given location. Solving the Schrödinger equation for an electron in an atom gives a set of wavefunctions that correspond to the electron's energy levels and spatial probability distributions. Note the dramatic difference from the Bohr picture: now the electron can be anywhere there is a nonzero $|\psi|^2$ which is almost everywhere. The concept of exact position does not apply in the quantum world, since particles cannot have their position and momentum specified exactly, in accordance with the Heisenberg Uncertainty Principle.

Why this matters

Let's apply the de Broglie wavelength equation to an electron. We know the mass of an electron is 9×10^{-31} kg. Now put the electron in an electric field caused by a voltage of 100 V. We know this will cause the electron to accelerate and gain some momentum. Specifically, the energy of the electron is: charge*voltage = e*V = 100 volts *1.6×10^{-19} Coulombs = 1.6×10^{-17} Joules. This is because the unit volts is equal to units of J/C. So now we have an energy of the electron accelerated across 100V, and from that we can get its velocity, v 6×10^{6} m/s. Next we can get its wavelength: $\lambda = h/mv = 6.6 \times 10^{-34} J^{*}s/(9 \times 10^{-31} kg * 6 \times 10^{6} m/s)$, which when we realize the units of $J = [kg][m^2]/[s^2]$ we see gives us $\lambda = 1.2 \times 10^{-10} m = 0.12 nm$ for this electron.



This figure is in the public domain (created by NASA).

Remember the electromagnetic spectrum from last chapter? That's light covering orders of magnitude of wavelength, only a sliver of which lies in the visible range (400-750 nm). But in order to use this light to see things, we must use a wavelength of light that is either equal or smaller in size to what we're trying to see. Otherwise the light simply won't pick it up (you can check out the physics of diffraction for more info on this, but for now, you can take my word on it). The correlation between the limit of what we can see and the wavelength of light we use to see it is why I like this other electromagnetic spectrum picture. On it is superimposed examples of objects the size of the given wavelength. If we want to use a type of light to see, say, a human, then we'd need to stay at or below wavelengths of 1 m since humans are about 1 m in size. That doesn't mean we can see in the microwave region, but that's just a limitation of our eyes not of what is possible with a type of light. With better eyes than ours, we'd be able to use microwaves to see people, but we wouldn't, for example, be able to use radio waves since they have a longer wavelength than the thing we're trying to see.

Now let's go to the atomic scale: at the x-ray part of the spectrum, we'd need to use x-rays or gamma rays to see objects at that scale. But it turns out that not only can our eyes not see in that part of the spectrum, but even the devices and detectors we've built cannot see all that well. We can take x-rays and do so all the time, but only to see images on the mm resolution as opposed to nm. For the latter, we'd need to see an x-ray reflecting off of a nm-sized object and be able to measure it with precision, something we're not able to do. That said, we do use x-rays to get atomic-scale information, but that's a different thing all together and it has to do with the spacing between atoms in solids. We'll learn all about that later in the semester. But here we're still trying to actually "see" the object and the object is an atom. We can't use x-rays—even though they're at the right wavelength—and forget about gamma rays, because they're even harder to detect. But what else could we use?

That's why we did the electron wavelength calculation to start this Why This Matters section –

using the fact that an electron is a wave, and by giving it the right velocity, we can make an electron have exactly the wavelength needed to see at the atomic scale. Electrons can be our "flashlight"! It also turns out they're a lot easier to capture and use to construct images than x-rays. This discovery jump-started the whole field of electron microscopy and changed the way we see matter. It was Don Eigler and Erhard Schweizer who showed in 1989 that by seeing individual Xe atoms, they could arrange 35 of them to spell their company's logo. This is definitely an expensive way to write a logo, but the point is that the accomplishment realized Richard Feynman's dream of being able to put an atom wherever you want.

Speaking of Feynman, he was an incredible scientist and a masterful teacher. If you want to see an amazing lecture entirely devoted to the double-slit experiment, find and watch Feynman's 1959 speech, "There's Plenty of Room at the Bottom," and you won't regret it. This is where he laid out the dream of putting atoms anywhere you want, and that was truly the first vision of the field we now call nanotechnology. The reason it took 30 years to realize Feynman's dream is that we were working in the dark, literally. If you can't see atoms and molecules, it's hard to control them or at least know that something you've done led to an atomic-scale control that you wanted. This type of control led to the nanotechnology revolution and it was entirely enabled by the ability of scientists to see materials at the nm scale, which as you now know was made possible by the wave nature of the electron.

Why this employs

It is true that we put humans on the human without resorting to quantum mechanics, evidence to how powerful and useful the classical view of the world is. But in order to truly understand the world, from the atom to the oceans and mountains to the universe to life itself, the quantum nature of it all must be understood and in some cases quantum effects completely dominate. Electrons and their interaction with light fall into this category: without a quantum description there's no hope in explaining the interactions that take place. So let's talk about jobs related to lasers.

Stimulated emission (first discussed in a paper by Einstein in 1917) involves the interaction between a photon and an atom that has electrons in an excited state. If the photon has just the right wavelength when it hits the excited atom, then the atom emits a second photon identical to the first. The LASER is "Light Amplification by Stimulated Emission of Radiation," and it is entirely and only described by quantum mechanics since it relies on knowing the discrete energies levels of electrons in the atom. And by the way, any time you're online, you're using a laser since that's how information travels through fiber optic cables.

There are so many job postings for "laser engineer" that it wouldn't be possible to even begin to list (one site I just checked has 7000+ listing!). The reason is that lasers are used today in every walk of life. There are jobs with lasers in medicine, like in eye surgery, to industry where lasers cut and weld, to tracking systems for all sorts of applications, to research in new types of spectroscopy, to so many many more. So if you want a job that uses wave-particle duality to make coherent light, then that's an awesome first step, but the next step would be to get more specific.

Take LIDAR as an example: this stands for Light Detection and Ranging, which is a remote sensing method that uses laser pulses to measure distances. LIDAR has completely revolutionized the ability of robots, like self-driving cars for example, to see. It's inside those bulky boxes on top of a self-driving car that spins continuously, giving 360 degrees of visibility as well as extremely accurate depth information (to +/- 2 cm). It's still expensive ($75K a pop for the car-top systems!), but because of how enabling LIDAR is, and how much the demand for this technology will grow, there are many jobs opportunities. These range from jobs at big player companies like Velodyne that's already selling systems to many markets, to smaller companies trying to innovate the technology like Luminar that promises a $500 LIDAR system in the size of a soda can. There's a whole range in between including self-driving car companies themselves like Waymo that have decided to build their own LIDAR systems. And this was just one tiny example of the vast number of LASER-based job opportunities.

Example Problems

1. You observe hydrogen electrons transitioning from n=3 to n=1.

a) What is the energy change in this transition? Is it absorption or emission?

b) What color light do you observe?

c) How many possible transitions could an electron falling from =3 to n=1 complete? Which transition is responsible for the orange color?

2. A red laser, a green laser, and a blue laser shine on different pieces of the same kind of metal, and detectors are set up to measure the presence of emitted electrons. For the red laser, no electrons are detected. For the green laser and the blue laser, electrons are observed flying off of the metal. Which of the following statements must be true?

i) The number of electrons emitted from the metal using the blue laser is greatest
ii) The kinetic energy of electrons emitted from the metal using the blue laser is highest
iii) The red laser would lead to electron emission if the laser intensity was increased

Solutions

1. a) The electron is falling to a lower energy state from a higher energy state, so it must be emission.

$$\Delta E = -13.6Z^2(\frac{1}{3^2} - \frac{1}{1^2}) = -12.09eV$$

We can double check our intuition: since the energy value we found is negative, the transition must correspond to emission.

b)

$$\lambda = \frac{hc}{10.2[eV]} = 1.22 \times 10^{-7}m = 102.6nm$$

This transition is in the UV.

c) There are two possible paths: straight from n=3 to n=1 or n=3 to n=2 + n=2 to n=1.

Next, calculate the wavelength of the three possible photon emissions. We already know that from n=3 to n=1, the wavelength of the emitted photon was 102.6nm.

From n=2 to n=1:

$$\Delta E = -13.6Z^2(\frac{1}{2^2} - \frac{1}{1^2}) = -10.2eV$$

$$\lambda = \frac{hc}{10.2eV} = 1.22 \times 10^{-7}m = 122nm$$

This transition is also in the UV.

From n=3 to n=2:

$$\Delta E = -13.6Z^2(\frac{1}{3^2} - \frac{1}{2^2}) = -1.89eV$$

$$\lambda = \frac{hc}{1.89eV} = 6.57 \times 10^{-7}m = 657nm$$

This transition corresponds to orange light.

2. ii) is true, because the blue light has higher energy than green and red light, and the energy of electrons emitted is proportional to the energy of the photons hitting the metal surface

i) and iii) are incorrect because the number of electrons is related to the number of photons = light intensity, and light intensity does not affect energy of electrons emitted.

Lecture 6: The Atomic Orbital and Quantum Numbers

Summary

One of the main limitations of the Bohr model is that it can only describe an atom with a single electron. To find the properties of multiple electrons in an atom, it is necessary to solve the **Schrodinger equation**, $(K+V)\psi = E\psi$, where K is kinetic energy, V is potential energy ($-1/r$ for an electron in an atom), E is the total magnitude of energy, and ψ is the **wavefunction**, or **orbital** of the electron. The solution to the Schrodinger equation for an electron in a hydrogen atom has three separate components: $\psi = R(r)P(\theta)F(\psi)$. The full form of the solution form has three big implications:

1. Electrons don't really orbit around atoms, at least in the sense that planets orbit around the sun. The solution to the Schrodinger equation yields a wavefunction, which when squared, gives an expression $|\psi|^2 = 1$for the probability distribution of the electron's location in relation to the nucleus. Further, though each electron has some radius it is most likely to be found, there is also a chance that it is much closer to or much further from the nucleus. For example, while Bohr model electrons with n=1 live at exactly 0.529 Å from the nucleus, the wavefunction for a real electron in the hydrogen atom has occupational probability peaked at 0.529 Å and smeared out on either side of that value. As the principle quantum number increases, the number of **nodes**—forbidden regions—increases, giving distinct bands around the atom where the electron is likely to be.

2. Four quantum numbers are necessary to fully describe a particular solution. The principle quantum number, n is primarily responsible for the energy level of the electron. Just like in the Bohr model, n can take any integer value from 1 to infinity. As n gets larger, the total energy gets less negative (bigger). An electron is equivalently referred to as being in the n^{th} energy level and the n^{th} shell; the remaining quantum numbers describe subshells. The angular momentum quantum number, l, is primarily responsible for the shape of the orbital. The values that l can take on depend on which shell the electron is in: the range goes from 0 to (n-1). The magnetic quantum number, m_l, is responsible for the orientation of the orbital in space. Its values depend on both n and l, and the range of m_l goes from (-l) to (l). Finally, the spin quantum number, m_s can have one of two values: +1/2 or -1/2, which is equivalently referred to as up or down.

3. Electrons that solve the Schrodinger equation are distinct from Bohr electrons. While there is only one electron per shell in the Bohr model, the Schrodinger equation gives degenerate solutions: as n increases, there are more and more orbital levels. Further, the Bohr model gives a fixed allowed radius for the electron to live, while the Schrodinger equation gives a distribution of probability that an electron is at a given distance from the center (and some forbidden zones!). Finally, though the Bohr model could only describe the behavior of one-electron atoms, the Schrodinger equation is much more broad: it can describe the electronic structure of an atom with any number of electrons.

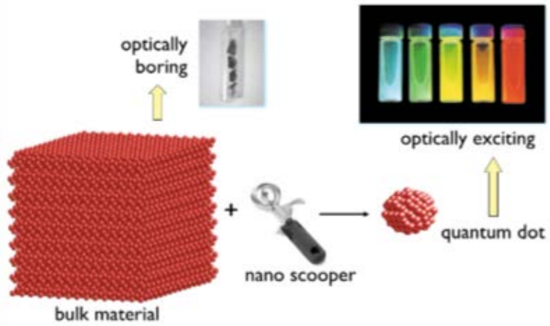
We also discussed how the values for the l quantum number get the letter names s, p, d, and f corresponding to $l = 0, 1, 2, 3$, respectively. If we say an electron is in the $2s$ orbital, then we know it corresponds to the quantum numbers $n = 2, l = 0, m_l = 0$, and spin could be up or down. Other examples of sets of quantum numbers and the corresponding orbitals were covered and these hydrogen orbitals were shown as the building blocks of chemistry. That's because to describe an atom and its properties, we fill these orbitals from lowest energy up, with the number of electrons Z in the atom. This occupation follows a general trend that is the topic of the next lecture, but in this one we covered a very important rule: the Pauli Exclusion Principle. This rule states that no two electrons can have the same set of quantum numbers, meaning that two electrons and *only* two electrons can occupy any given orbital.

Why this matters

Quantum weirdness is one of the most important reasons why nanotechnology has gotten so much attention recently. Now, there has been quite a bit of press about nanotechnology over the last two decades, but one of my all-time favorite articles appeared long ago in the U.K. Telegraph: "How Super-Cows and Nanotechnology will Make Ice Cream Healthy." I always remember that piece because of the way they define nanotechnology: they describe a company as "experimenting with nanotechnology, or the science of invisibly tiny things." I suppose I like this quote because of how ridiculous it is, since first of all there are many different realms of science and engineering associated with tiny things we cannot see (nanotechnology is one of them, but how about nuclear physics with its quarks and gluons, or solar wind with its hot plasma particles that reach our earth only to be deflected by our planet's magnetic field, or dark matter?). Second of all, I like this quote because it shines a spotlight – albeit incorrectly – on one hold-up in nanotechnology development, which was not being able to observe what was happening. This changed once we could use electrons as a way to illuminate matter, as discussed in last chapter's Why This Matters.

The main point is that nanotechnology holds great promise. Not so much for the reasons that gave it fame in the early 2000's (healthy ice cream being the least of it, we were supposed to have a space elevator by now!), but rather because of the chemistry that's "under the hood" of nanotechnology. What does nanotech even mean, and why do we have a whole name for it? Let's answer that with an example directly related to today's lecture.

We've been talking about orbitals of electrons in atoms and how the orbital is the probability cloud for the electron. Well what if we take that cloud, and we squeeze it? Or in other words, confine it so that it can't take up the same volume as it typically would. There's a name for that: quantum confinement. And when we confine quantum things, like in this case an electron in an atom, new properties emerge. Take color as an example. For a piece of bulk material, where "bulk" here just means it's not nano-sized, I might have something that's kind of optically boring. It's just a piece of gray material. But then I take out my nano-ice-cream-scooper and I make a little tiny chunk of the material. Suddenly, without changing anything except the size, I can tune the color to pretty much anything I want!



Images of bulk semiconductors, ice cream scoop, quantum dot © sources unknown.

The fact that changing the size of this material allows us to tune a given property is quite incredible. Imagine if I were to take one of those strips of metal from your first Goodie Bag and break it into two pieces: you wouldn't expect the color of the metal to change. But if you could break just a tiny piece of it off, like one with just 10-20 atoms in it, then that piece would change color. How weird is that? It's because of this electron cloud running out of real estate when the amount of matter is small enough. When it's nanoscale, the confined probability cloud changes the energy of the electron, which in turn changes the color of the material. We talked about electrons changing their energy levels in atoms as a way to either absorb or emit a photon corresponding to that energy shift. Well here we've got a new way to shift the starting and terminating levels themselves, simply by changing the size of the material. That's an example of why nano is such a big deal.

The ability to control the properties of a material is one of the foundations of our modern era. As we've already learned, understanding the periodic table of the elements and all of the differences between the behavior of these elements gave scientists and engineers knowledge of the basic ingredients that are used to build our world. Going nano is kind of like adding a whole other dimension to the periodic table: it's like each element can now do new things, take on new properties, and be utilized in new applications.

Why this employs

Quantum computing has gotten a lot of attention recently, and for good reason. Over the past decade, we have reached the point where quantum bits, or qubits, can be made and controlled experimentally. The computers we use today manipulate information in the form of individual bits, which are the famous 1's and 0's of the last 50+ years. But in a quantum computer, the quantum mechanical phenomena that we've been learning about in this chapter are used to manipulate information.

It's qubits that hold the key since those are the keepers of quantum states, which have quantum numbers just like the electron states in an atom. When two qubits interact with one another we get much more than just 1's and 0's, instead we get all possible superpositions. It's like being able to harness the probability cloud as a computing cloud where all possible answers are computed at once.

Quantum computing is getting a lot bigger and a lot more exciting, with many companies predicting commercial quantum computers by 2025. The Why This Employs idea for this lecture is to take those quantum states we've just discussed and run with them... all the way to Google's Artificial Intelligence Lab, or to the team at IBM Q, or to D-Wave, or to the folks at Intel working on their Qubit Chips, or to any of the 63 companies currently listed at Wikipedia under "Companies worldwide engaged in the development of quantum computing." A list that is growing rapidly. And that doesn't even include doing research on this topic in a lab here at MIT :)

Example problems

1. Write the quantum numbers for each electron in a neutral carbon atom.

Solutions

1. Note: the spin signs are selected arbitrarily, so it would be just as correct to flip them all. For

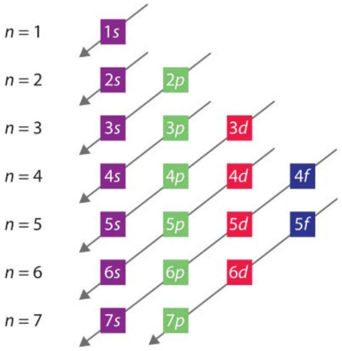
n	l	m	m_s
1	0	0	1/2
1	0	0	-1/2
2	0	0	1/2
2	0	0	-1/2
2	1	-1	1/2
2	1	0	1/2

the 2p electrons, they must have the same spin due to Hund's rule.

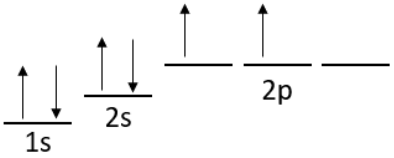
Lecture 7: Filling the Periodic Table and Our First Bond (it's Ionic)

Summary

The **Aufbau principle** is a tool used to remember the (typical) order in which subshells are filled in a multielectron atom. Electron interactions complicate which subshells are filled first: shielding and orbital penetration affect which combination of electron energy and shape (quantum numbers n and l, respectively), is the next-most-stable state. The Aufbau principle is often represented visually. Though the Aufbau principle generally gives the order that electrons fill in the subshells, it doesn't tell the full story. Previously, we learned that each orbital can hold two electrons: one spin up and one spin down. We also learned that each value of l, written here as s, p, d, and f, can have a different number of subshells based on the allowed values of m_l. The **electronic configuration** of any atom can be written using these guidelines: for example, potassium is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$. Often, the electronic configuration is shortened to include only the nearest fully occupied noble gas atom and the valence electrons: in this case, potassium is [Ar] $4s^1$.



When an atom has only a partially filled shell, **Hund's rule** comes in to play: all of the orbitals in the partially-filled subshell must be singly occupied before any are doubly occupied. For C, which has 6 electrons and electronic configuration $1s^2 2s^2 2p^2$, Hund's rule tells us that the electrons are distributed as shown in the diagram below.



If the elements are arranged by increasing number of electrons (and protons), **periodic trends** start to emerge, and electron filling explains the organization of the Periodic Table with blocks that correspond to the subshell being filled. The s- and p-blocks are "main group" elements while those in the d-block are "transition elements" and "f-block" are "inner transition elements." A larger principal quantum number n corresponds to bigger orbitals and therefore bigger atoms: from this, we can predict that atomic radius should increase down a period in the periodic table. On the other hand, having more protons pulls electrons in towards the atom, so atomic radius gets smaller going from left to right across a row. If an atom loses an electron, its radius decreases: this kind of atom is called a "cation." Similarly, if an atom gains an electron, the "anion" is bigger.

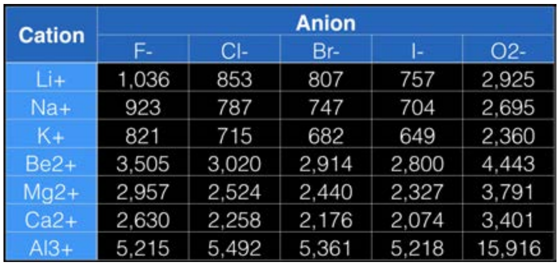
Finally, we learned that ionic bonds are the electrostatic attraction between two oppositely charged ions: they're formed by the transfer of one or more electrons between the ions. The strength of an ionic bond can be approximated by a Coulomb interaction: $E = kQQ/r$. If the distance between two ionically bonded atoms is greater, the bond will generally be weaker! Just by looking at the size of the ions that make up the bond, we can infer a lot of information about the corresponding ionic solid.

Orbital filling diagram (upper right) by B.A. Averill & P. Eldridge in *Chemistry*. License: CC BY-NC-SA. Source: Open Textbook Library.

Why this matters

We just made our first bond in 3.091, and it's a strong one! Take a look at this table of lattice energies (in kJ/mol) for a bunch of ionic solids. The range of ionic bond strength spans an order of magnitude in this chart, but even the weakest solid listed (potassium iodide, KI, at 649 kJ/mol) is still really strong with a melting temperature of 681°C.

The strongest ionic solid listed in this table is aluminum oxide, formed by combining 2 Al atoms for every 3 O atoms (this balances charge with Al being 3^+ and O being 2^-. Aluminum oxide melts at a whopping 2,072°C, and its widely used for its hardness and strength. For example, Al_2O_3 is used as an abrasive, including as a much less expensive substitute for diamond, and in many types of sandpaper or cutting tools. Because of its strength, it's used as an additive in many applications, including toothpaste! For this Why This Matters moment, I'd like to focus on an unfilled need rather than an established solution. This is a problem where a harder material with the right properties and in the right structure could change millions of lives.



Cation	Anion				
	F-	Cl-	Br-	I-	O2-
Li+	1,036	853	807	757	2,925
Na+	923	787	747	704	2,695
K+	821	715	682	649	2,360
Be2+	3,505	3,020	2,914	2,800	4,443
Mg2+	2,957	2,524	2,440	2,327	3,791
Ca2+	2,630	2,258	2,176	2,074	3,401
Al3+	5,215	5,492	5,361	5,218	15,916

Hemodialysis is a process to purify the blood of a person who has kidneys that don't work correctly. A typical patient will have to go in 3 times per week, sit in a chair that looks something like this for about 4 hours per session, totaling 600 hours of their time and a cost of $80,000 per year. In the U.S. alone there are 650,000 people who undergo hemodialysis, and this number has been growing steadily over the past 30 years. It is expected that, as the incidence of cardiovascular diseases such as diabetes and hypertension increase, the population of individuals needing dialysis will grow as well. That machine on the left of the chair in the picture is a hemodialysis machine. During the process blood is removed from the body through an access point in a patient's vein, and passed through the machine which removes toxins and excess fluids, after which the filtered blood is returned to the body through another access point back into circulation. Here's Why This Matters.

If that machine could be shrunk down to a much smaller size and made portable, then patients would be able to do this at home or while traveling or wherever they are, which would seriously improve their quality of life. But current filters don't work well enough to make the device small and portable, so people who need hemodialysis treatment are stuck. That is, unless a new filter could be invented, one that satisfies three key criteria: 1) the material must be biocompatible, 2) it must allow for selective filtration so it can remove some things but not others, and 3) it must provide efficient and fast filtration. Such a filter does not currently exist. Current filters are cellulose-based porous membranes with highly variable pore size, meaning that molecular selectivity is difficult to control. The pores in current filters also overlap a lot, making tortuous paths that slow the fluid motion, increasing the amount of time it takes for the blood to flow through. Current filters are easily clogged, they're delicate and tough to clean, so at best they're single-use only and at worst they get clogged so much so quickly that even achieving a single use is difficult.

Here we can consider the strong ionic bonds we learned about in this lecture. Here's a picture of a new filter made out of Al_2O_3. Note from the scale bar that the pores are seriously small, only 10s of nanometers in diameter. They're also aligned in the same direction (so none of that tortuous flow slowing things down), which means the flow through them will be fast and efficient. And note that the pores are all roughly the same size, which gives the filter the ability to sharply reject the targeted toxins. And of course, since it's a strong ionic solid, this filter can be cleaned very aggressively with pretty much whatever cleaning chemicals or thermal treatment you care to throw at it. There's still much work to be done, like reducing the cost of making such filters, and they're still a bit too brittle, but in general ionic solids hold tremendous potential as next-generation filters!

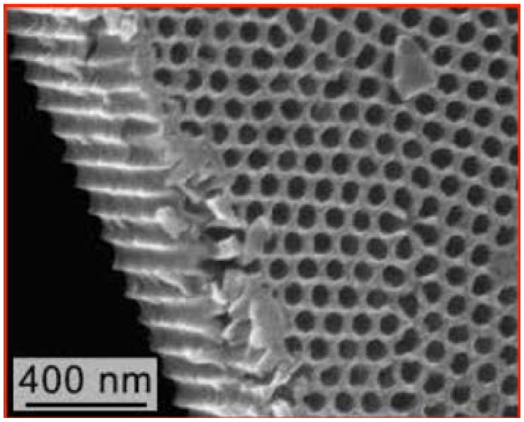


Image of alumina filter by Assaud, L. et al. *Beilstein Journal of Nanotechnology* 5 (2014): 162-72. License: CC BY.

Why this employs

That example of a new type of ultra-resilient filter is only one of many where new high strength materials are needed. And it's not just the material itself but also the way it's processed. And because of how badly resilient new materials are needed, many of the larger chemical companies like Dow, Saint-Gobain, BASF, Sinopec, LG Chem, Arkema, or Mitsubishi Chemical, to name just a few of the giants (all of these have annual sales in the $10's of billions.

And all of these companies have large teams working on making high strength materials. Sometimes it's high strength steel, sometimes it's plastic, and of course other times, ionic materials. All of these companies have job postings, but an excellent way to explore career interest is to do internships, and all of these companies also have internships for students. You could go directly to the company web site, or you could also check out the resources we have here at MIT. There are a lot of them.

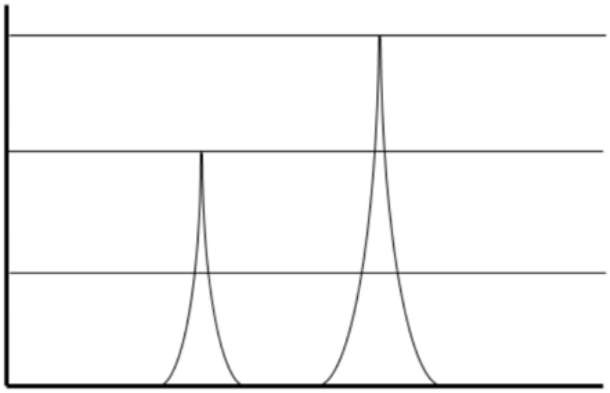
For example, take a look at the web page capd.mit.edu, where if you click on "Jobs and Internships" you'll get all sorts of support and resources. Definitely worth checking out!

Example Problems

1. Rank the following atoms in terms of size, ionization energy, and electronegativity:

Ge Rb Sn I

2. Below is a PES spectrum for the outer electrons of a mystery element. Label the axes and the direction of increasing ionization energy.



a) If the configuration of the inner electrons of the mystery element are the same as neon, identify the element.

b) Separately, while you were taking PES spectra for carbon in a vacuum, the seal on the vacuum machine broke and let in an unknown gas. You observe the following on the contaminated spectrum:

- i. There are 6 peaks total (including the carbon peaks)
- ii. Five peaks are the same height
- iii. One peak is three times higher than the others

What is the contaminating element? Explain your reasoning.

Solutions

1. As the period increases down the periodic table, electrons are more and more shielded from the nucleus, so atomic size increases. Additionally, as the group number increases across the periodic table, there are more and more protons and therefore increased attraction from the nucleus, so atomic size decreases.

(smallest) Ge I Sn Rb (largest)

2. a) Phosphorous: its electronic configuration is [Ne]$2s^2 3p^3$

b) The electronic configuration of carbon is $1s^2$ $2s^2$ $2p^2$. Since there are 2 electrons in each shell, these three peaks must be the same height. The additional peaks must therefore belong to $1s^2$ $2s^2$ $2p^6$, since one of the peaks is three times higher than the rest. The contaminating gas is Ne.

Lecture 8: Ions, Ionization, and Valence

Summary

This lecture we continued our discussion of ionization energy. We saw that, similar to Li and Be in the last lecture, the ionization energy for the elements along the periods (from left to right on the periodic table) in the p and d block increases due to a higher number of protons leading to an increased nuclear pull. It makes sense that more energy is necessary to free them. On the other hand, going down the groups (from the top to bottom on the periodic table) the ionization energy decreases because the increased shielding and distance from the nucleus is more significant than the increased nuclear pull due to added protons.

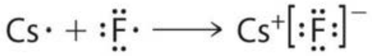
The reason for increasing ionization energies for electrons closer to the nucleus is that these electrons are more tightly bound. For example, Li's first ionization energy is 5.4 eV, while its second ionization energy is 122 eV. This second electron experiences less shielding than the first. This ionization energy information can be viewed on a **Photo-electron Spectroscopy** (PES) plot. This is a plot showing ionization energy versus relative intensity for a given element. PES involves shining enough energy on an atom to ionize all of its electrons, measuring their kinetic energy, with the difference being equal to how much energy the electron was bound by. PES is a simple, powerful technique to directly measure electron occupation.

Another periodic trend discussed was **electron affinity**, or the change in energy that accompanies an additional electron. The halogens (group 17 on the periodic table) have the highest electron affinity, because an additional electron would result in a full octet and complete filling of the subshell. Electron affinity increases along the periods of the periodic table up until the halogens.

This lecture also laid out the idea of **valence electrons**. These are the electrons that occupy orbitals beyond the highest filled noble gas core. For example, carbon and silicon both have 4 valence electrons. Carbon's highest filled noble gas core is [He], while silicon's is [Ne]. Valence electrons are what drive chemical bonds. Valence electrons on atoms are depicted using **Lewis Dot Diagrams**, which are the chemical symbols of the elements with dots surrounding them that represent the valence electrons. Lewis Dot Structures are helpful in visualizing the **octet rule**, which states that atoms (ignoring the transition metals for now) are at their lowest and most stable energy state with 8 electrons in their valence.

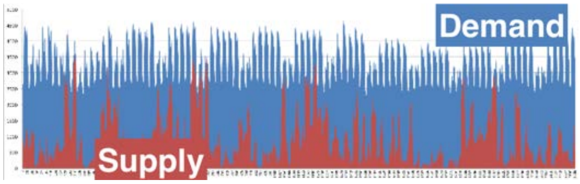
Figure removed due to copyright restrictions. Lewis Dot Diagrams of Selected Elements on Hyperphysics website.

In this lecture we began applying Lewis Dot Structures to ionic bonds. Cations are depicted with plus signs on their top right corner, and anions with negative signs, as shown below.



Why this matters

In this lecture, we've been focusing on atoms that lose or gain electrons, also called ions. Now we'll discuss how this topic relates to renewable energy solutions.



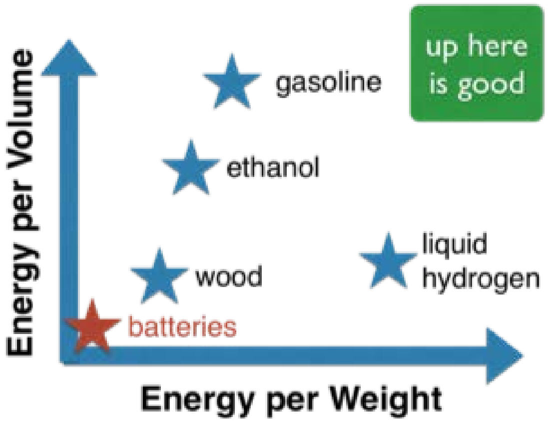
Take a look at this plot of the demand of electricity (in blue) vs. supply of electricity from a wind farm (in red), recorded over a two and a half month period in 2013 in Denmark. Notice that on the demand side, there's some variability, but there's also a lot of regularity. The 5-day work week draws more energy than the weekends, and the amount of energy needed doesn't really vary much from week to week. Now contrast that with the supply of electricity from a wind turbine farm. Even if you put the turbines in a known windy area, there's still a huge amount of variability. Wind energy is not that expensive to produce, but the biggest challenge isn't cost, it's steadiness of supply. If you think about how to build enough of this type of unreliable supply to meet the consistent demand, you'd need to overbuild capacity by a factor of at least 10 (and even that wouldn't be enough on some days)! That of course isn't going to be economically feasible, so the real solution, if we want to expand how much energy we get from intermittent renewables like wind and solar, is to be able to store the energy for when it's needed. If we have reliable storage, then the supply can be quite unreliable and we'd still be able to meet a steady demand, as long as on average the supply can meet it.

One of the easiest ways to store energy is to push something up a hill and then let it roll back down. Push a ball up a hill and then hold it there, and when you want the stored potential energy back as kinetic energy, simply let it go. We pump water up hills, called "pumped hydro," which is currently one of the only viable technologies that can scale up to the size (meaning, power) of actual electricity grids. A massive amount of water is pumped up a hill when there's excess energy supply, and then rolled back down to turn a turbine to generate electricity when there's excess demand. Although this is a relatively cheap storage solution, there are all sorts of problems with scaling up any further than it is today, primarily because of the low energy we get from gravitational energy and therefore how much land is required. There's a great post that explains why it will be hard to increase pumped hydro as an energy storage technology at dothemath, which is a cool site in general if you haven't seen it: https://dothemath.ucsd.edu/2011/11/pump-up-the-storage/.

So what else can we pump up a hill to store energy? This is where our ions come into the picture! Ions are the key ingredient in batteries. Think of a battery as an electronic hill, and when the battery is charged the ions are getting pumped up. Cations in particular, like Li+, get pushed up the energy hill, and the lower energy state (down at the bottom of the hill) would be one in which it can get that electron back and become neutral again. When the circuit is closed, the cation falls down the energy hill to meet up with the electron, which goes around the circuit doing work along the way. In this case instead of mechanical work like the water, the electron is doing electrical work directly. This is one of the great advantages of electrochemical storage (a nice way of saying a battery), namely that we're storing directly the kind of energy we mostly need, electrical energy. Stored mechanical or thermal energy later often needs to be converted into electrical at great efficiency loss.

But how good are batteries today, really? Could they ever be used to store the massive amounts of energy needed at “grid scales”? For reference, the U.S. uses 3 TW on average, or 3x10^{12} Watts = 3x10^{12} Joules/second of energy, so you get a sense of what it means to be at the scale of the grid. Let’s make sure we’re straight on energy vs. power: a Watt is a Joule/second which is energy per time, which is power. That’s an important metric since we need to be able to access energy at a given pace. The total amount of energy is power multiplied by time, so for the U.S. if our average power draw as a nation is 3 TW, then our daily energy use is 72 TW-hours (TWh) and our yearly energy use is 26,280 TWh. Just to give you a sense of how big this number is, a typical AAA battery stores about a single Wh of energy. That means if we wanted to store the U.S. energy needs all we would need to do is build a storage facility containing 26,280,000,000,000,000 AAA batteries! In case you’re wondering, that’s about a million times the number of AAA batteries sold in the U.S. each year.

And therein lies the problem with batteries, namely their low energy density. But as I hope you’re seeing in this class, such problems are often opportunities for chemistry to come in and make a game-changing difference.



This figure shows the energy per weight vs. energy per volume for a few different storage materials. Note that batteries are in the lower left, which isn’t so good. You can see why gasoline is so unique: it’s got a very high energy density both by weight and by volume, and on top of that it’s safe and easy to transport and extremely cheap. The competition is tough.

One liter of gasoline stores 33 megajoules (MJ) of energy, or about 9 kWh if you prefer those units. That liter costs about a dollar. Now take one MIT Professor, who can output about 60 W or 60 J/s on a good day. This means that the professor can generate the same amount of energy as in a liter of gasoline, 33 MJ, in roughly 153 hours. Given the average pay of an MIT professor of \$10/hr, it would cost \$1530 to get the energy from the professor. Compared to about \$1 to get the same amount of stored energy from the gasoline. Batteries need to start looking a lot more like gasoline and a lot less like an MIT Professor if they’re going to be competitive grid-scale energy storage technologies.

The good news is that there has already been tremendous progress in just the last 10-20 years. Check out this plot of energy density vs. year for batteries. Notice the very slow progress for about

150 years, with a doubling of energy density occurring roughly every 60 years. Then the slope of progress changes, and the reason is simple: chemistry. Specifically, the rapid improvements are happening because we've reached an era wherein we can make energy hills for ions with many more types of materials than ever before. I've added to the plot the number of materials cathodes are made of: historically only about 10 different cathode materials were used during those slow-paced first 150 years, but now we can and do make cathodes out of over 80 different materials, and the number is growing by the week. This explosion of materials possibility is due to a deeper understanding of ions and new ability to design materials with more efficient energy landscapes for them to traverse. So yes, there's a lot of work to do to make batteries competitive in grid-scale energy storage, but the time is absolutely ripe to get it done.

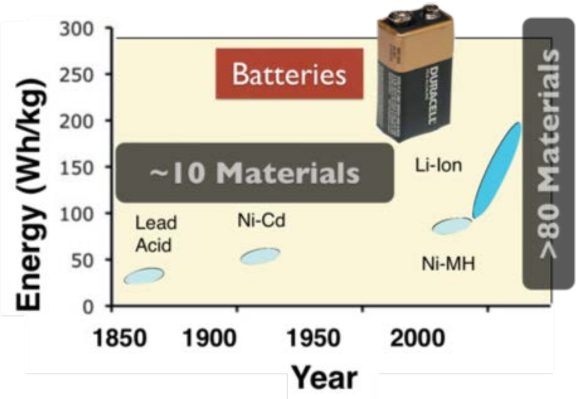


Figure energy vs. year © source unknown. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/fairuse.

Why this employs

Knowledge of ions can get you all sorts of jobs. But since I focused on the battery field in Why This Matters, let's focus on that same topic here. The global battery market is already enormous and its projected growth is stunning. Here's a chart from a report from Deutsche Bank from 2016 showing the projected near-term growth in battery production by some of the top companies that make batteries. All of these companies are hiring thousands and thousands of scientists and engineers, techno-economists (predicting tech trends is not easy!), packaging and mechanical design experts, and much more, all to work on various aspects of one thing: the ion. And there are many more jobs than that. Big battery companies like those listed in the chart are investing heavily in hiring people to work on batteries, but so are little companies. And so are many research teams at universities, who are spinning out companies based on new concepts.

Not only are there many different battery chemistries that have been around for a while and are being greatly improved, from lithium-ion to nickel-metal-hydride to lead-acid, but there are also so many exciting completely new directions for batteries. All of these future battery technologies involve jobs, and while it's hard to list them all because of how much the field has grown, here are a few cool directions companies are pursuing:

- Silicon-based anodes (replacing the currently used graphite) which would increase energy density by a factor of 3
- Using metal nanowires in the electrolyte to prevent breakdown, making the battery last 10 or 100x longer

New Battery Capacity figure removed due to copyright restrictions.

- Making the electrolyte a solid instead of the current liquid, which would make the battery more stable and allow much faster charge times
- Throwing graphene into the battery since, anyway, what problem can graphene not solve? (ok, but in all seriousness, graphene has been shown to allow for much faster charge/discharge)
- Making batteries out of foam metals
- Making batteries foldable (paper-thin but that won't break) and also stretchable
- Aluminum air batteries that have demonstrated a 1,100 mile range in an electric car
- Powering the charging of batteries with variou means, from wi-fi signals (not inductive wireless, which is something else), to ultrasound, to amino acids, to urine.
- Batteries made from sodium, zinc, sulfur, magnesium, and so many other materials!
- Making batteries that can never catch fire

Example problems

1. Choose the larger atom from the following pairs:

a) Rb, Rb^+

b) Rb^+, Kr

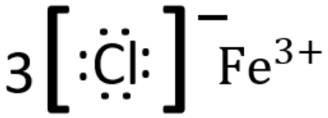
2. Draw the Lewis dot structures of $FeCl_3$ and MgF_2.

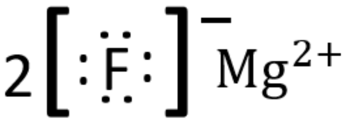
Solutions

1. a) Rb is larger, because it has an additional shell (Rb^+ loses its $5s^1$ electron)

b) Kr is larger, because it has one less proton than Rb^+, so the nucleus pulls less on the electrons

2.





Lecture 9: Lewis Structures, Covalent Bonds, and Resonance

Summary

H-H H-Cl Cl-Cl bonds diagram removed due to copyright restrictions.

Covalent bonds are created via the sharing of electrons rather than through electrostatic attraction between cations and anions, as in ionic bonds. The shared electrons in covalent bonds achieve a lower and more stable energy state by interacting with two nuclei instead of one. Lewis Dot Structures represent the two electrons in a covalent bond with lines, as shown for H_2 to the right.

To represent more complex molecules using Lewis Dot Structures, the following set of rules come in handy:

1. Connect atoms, central often less electronegative
2. Determine total number of valence electrons
3. Place bonding pair of electrons between adjacent atoms
4. Starting with terminal atoms, add electrons to each one to form octet (2 for H)
5. If electrons are left over, place on the central atom
6. If central atom hasn't reached octet, use lone pairs from terminal atoms to form multiple bonds to the central atom to achieve octet

It is possible to have more than one Lewis structure that doesn't valuate the octet rule. For these instances, we calculate the formal charge. The sum of the formal charge must equal the overall charge on the molecule or ion. To calculate formal charge, follow these steps:

1. Nonbonding electrons are assigned to the atom on which they are located.
2. Bonding electrons are divided equally between the bonded atoms.
3. Then, the formal charge can be computed for each atom as follows:

$$formal\ charge = valence\ e^- - \left(nonbonding\ e^{-\prime}s + \frac{bonding\ e^{-\prime}s}{2}\right)\Bigg($$

In addition to stability, formal charge tells us about the structure's electronegativity—atoms with negative formal charge should be more electronegative, and those with positive formal charge less electronegative.

It's also possible to have two different Lewis structures with the same formal charge. This indicates that the actual molecule is a combination of its most stable resonance structures, as with the ozone example in class, where we have on average 1.5 bonds on either side of the center oxygen.

We also discussed the concept of **polarity**—a measure of how unequally electrons are shared between two atoms in a bond. In nonpolar covalent bonds, the electrons are shared equally, as in H2.

In polar covalent bonds, the sharing is unequal. **Electronegativity** (χ), the tendency of an atom to attract a shared pair of electrons toward itself, can be used as a measure of polarity in a bond. In a completely nonpolar bond, the two atoms will have identical electronegativities, meaning $\Delta\chi = 0$. In a strong ionic bond, there is a large difference in electronegativities. In CsF, using Pauling's scale, $\Delta\chi = 3.98 - .79 = 3.19$.

Finally, we named some ways that the octet rule can be broken. Some elements, like boron, can have fewer than 8 electrons. Others, like sulfur, can have an **expanded octet**.

Why this matters

Speaking of the CO_2 molecule and its formal charges and stable structure, that's the focus of this Why This Matters. Let's get this done up front: after a century and a half of experiments and data collection, the scientific community has established with enormous consensus that carbon dioxide emissions are the primary cause of climate change. Other theories such as solar cycles or volcanic activity do not correlate with observed temperature changes, and there is now only one consistent explanation for rising global temperatures and our changing climate: anthropogenic greenhouse gases, led by carbon dioxide.

By the way, if anyone (say, I don't know, a politician?) were to tell you something like, "There is tremendous disagreement as to whether the earth is round. The debate over the earth's shape should be encouraged — in classrooms, public forums, and the halls of Congress," you would call such a remark either obliviousness or a lie. This is the same kind of lie told by many people about the facts of climate change. A great deal of media coverage focuses on how to define such "alternative facts," but categorizing the remark is beside the point. Regardless of what we call it, this type of statement is a threat to the very foundations of science, to reason-based argument, and therefore to society. Politicians may live in a "post-fact" world, but scientists do not, and cannot. There is no "post-fact science."

Ok, back to our molecule. Why is this particular molecule so important for climate change and global warming? CO_2 is called a "greenhouse gas" because of its ability to absorb infrared radiation, which in turn warms the planet. Take a look back at the plot of intensity of solar radiation hitting the planet as a function of frequency, from Why This Matters in lecture 4. Yellow is what strikes the upper atmosphere and red is what hits earth's surface, so the difference between the yellow and red curves is where some of that solar energy is being absorbed. Small molecules in the atmosphere, like ozone, water, and carbon dioxide, are what absorb that incoming solar energy. You can see where CO_2 is absorbing, out towards the right in the infrared part of the spectrum, while ozone is over on the left in the UV, and water is everywhere. It's the strength of IR absorption that makes CO_2 such an effective greenhouse gas.

About 25% of the solar radiation that hits the earth (so 25% of the integrated red in the plot) gets reflected back out to the universe. But what is reflected is not what is absorbed: instead, most of the energy that is reflected is in the longer wavelength, infrared part of the spectrum. Since CO_2 absorbs efficiently in that part, it acts like a blanket, keeping some of that reflected energy from escaping and redirecting it back to the atmosphere and surface. This blanket keeps us at a cozy 15°C instead of -18°C, which is what the average temperature on earth would be if all of that reflected solar energy were able to escape.

As an aside, the term "greenhouse gas" is a bit of a confusing name that has unfortunately stuck. The effect of absorbing long wavelength radiation on the planet's temperature has nothing to do with the effects of warming in a greenhouse used to grow plants, the latter relying mostly on preventing air convection from carrying heat away.

Here's the connection back to our Lewis structures and formal charge. That efficient absorption of CO_2 in the infrared I mentioned, that is directly related to how the atoms in the molecule vibrate. The photon is absorbed because it gets transferred into vibrational energy, so the specific way atoms jiggle around is extremely important to what photons it can absorb and how efficiently it does so. If the CO_2 molecule were to have a triple bond and a single bond, which is a valid Lewis structure but with higher formal charge, then its patterns of vibrations would change dramatically compared to the more stable double-bond case (with formal charge=0), which in turn would make it much less efficient at absorbing all the infrared energy!

Why this employs

Today's lecture has been about the covalent bond, a convenient way to represent it with Lewis structures, and what we can learn about molecules from these structures. It's hard to come across a job in any engineering or science field that doesn't require at least some understanding of the covalent bond since it's so ubiquitous. This also makes it hard to zero in on a specific job market for Why This Employs. That's why I'm going to focus way down to a single material – carbon – and the jobs you could find related to its covalent bonds.

In a few lectures we'll be learning about molecular orbitals and as an example you'll see just how flexible carbon can be in its bonding environment. It's one of the most flexible elements in the whole PT in that it likes single, double, and triple bonds as well as anything in between (read: resonance structures and delocalization). Let's pick one of the many forms carbon takes to focus on here: the aromatic ring. The term aromatic does have its origins in the fact that aromatic molecules can have a sweet fragrance to them, but in fact benzene—the classic aromatic molecule— has no such smell. Instead, the way the term is used in chemistry is that the electrons in a ring of carbon have lowered their energy by delocalizing (yes, resonance structures!). Most often this occurs for a ring that has alternating single and double bonds, which then form an average over its resonance structures. Benzene is the classic example of this, as it is the simplest aromatic ring one can make.

And you've probably heard of benzene before, but what you may not know is just how many ways benzene can be modified to make or do something useful. Check out this chart of only a very small fraction of benzene derivatives, where the ring has some addition(s) to give it a specific property or functionality. This massive variation of the chemistry of a single molecule is possible largely because of that covalent bond that carbon makes.

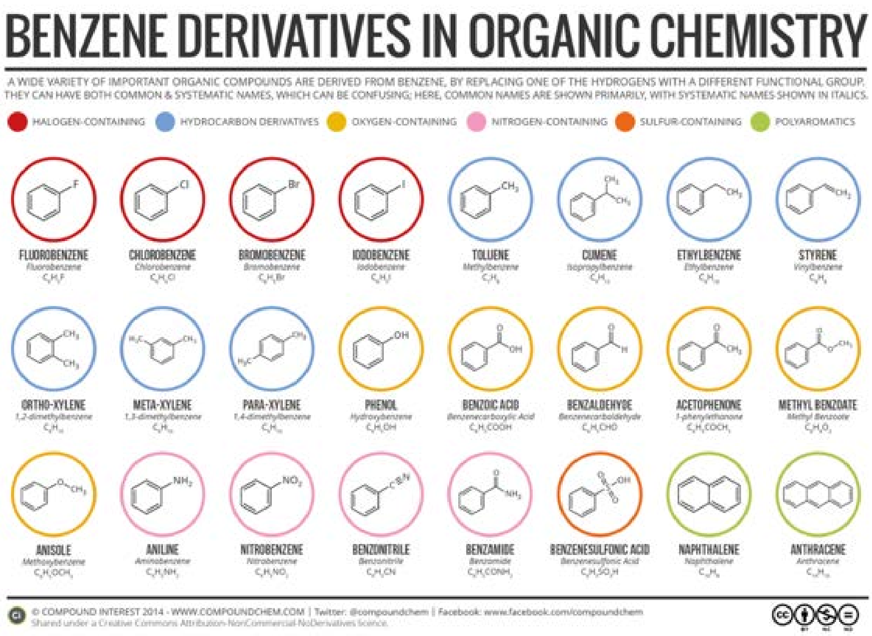


Figure of benzene derivatives by Compound Interest 2014 - www.compoundchem.com. License: CC BY-NC-ND. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/fairuse.

Many materials we encounter on a daily basis are manufactured from derivatives of benzene. Polystyrene, for example, is a polymer formed by connecting styrene molecules together, and billions of kilograms of polystyrene are produced each year. So, certainly jobs in companies that involve manufacturing, recycling, or utilizing plastics like polystyrene are related (I'm thinking a senior chemist position at BASF, a chemical manufacturing company, for example). But the uses of benzene derivatives go far beyond plastics. For example, industries use benzene to make resins, nylon and many different synthetic fibers, as well as lubricants, rubbers, dyes, detergents, drugs, and pesticides. Take medicine as another example: here's the acetaminophen (Tylenol) molecule – it's a benzene derivative!

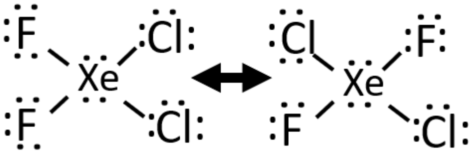
3-D image of acetaminophen molecule removed due to copyright restrictions.

So the pharmaceuticals industry is also a great place to take your knowledge of benzene (I'm thinking Johnson and Johnson, Pfizer, Novartis, and so on). These companies invest billions and billions of dollars every year to fund research on the development and testing of new medicines, many of which have at their core a resonant Lewis structure.

Example Problems

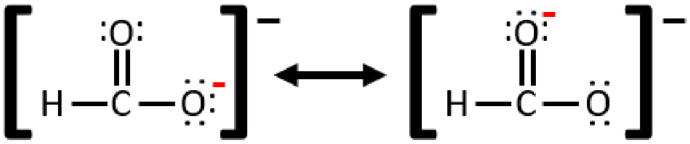
1. Draw the resonance for $CHO_2{}^-$ and assign formal charges to each atom.

2. True or false: The following picture shows two resonance structures of a molecule



Solutions

1.



2. False. The two structures aren't resonant structures because the atoms move around.

Further Reading

Lecture 1: Introduction and the chemistry of the periodic table

- History of atoms (not tested):
https://courses.lumenlearning.com/trident-boundless-chemistry/chapter/history-of-atomic-structure/

- Balancing reactions and limiting reagent:
https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_(Inorganic_Chemistry)/Chemical_Reactions/Limiting_Reagents

Lecture 2: Counting Atoms and Organizing the Elements

- The mole and molecular weight:
https://opentextbc.ca/chemistry/chapter/3-1-formula-mass-and-the-mole-concept/

- More info on careers in food science and agricultural chemistry:
https://www.acs.org/content/acs/en/careers/college-to-career/chemistry-careers/agricultural-and-foo
html

Lecture 3: The Discovery of the Electron and the Structure of the Atom

- Review of isotopes:
https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Atomic_Theory/Isotopes

- Plum pudding recipe (not tested):
https://www.epicurious.com/recipes/food/views/superb-english-plum-pudding-20010

Lecture 4: The Bohr Model and Electronic Transitions

- More on Black Body Radiation, quantization, and a cool video on the photoelectric effect:
https://chem.libretexts.org/Courses/University_of_Arkansas_Little_Rock/Chem_1402%3A_General_Chemistry_1_(Belford)/Text/6%3A_The_Structure_of_Atoms/6.2%3A_Quantization%3A_Planck%2C_Einstein%2C_Energy%2C_and_Photons*

- Summary of emission and absorption spectra:
http://physicsnet.co.uk/a-level-physics-as-a2/electromagnetic-radiation-quantum-phenomena/line-spectra/

- Science in context—Einstein and other prominent scientists fled Nazi Germany (not tested):
https://physicstoday.scitation.org/do/10.1063/PT.6.4.20180926a/full/

Lecture 5: Wave-Particle Duality and Quantum Mechanics

- More on wave-particle duality and the quantum atom:
https://www.khanacademy.org/science/physics/quantum-physics/quantum-numbers-and-orbitals/a/the-quantum-mechanical-model-of-the-atom

- Photoelectron spectroscopy:
https://www.khanacademy.org/science/chemistry/electronic-structure\-of-atoms/electron-configurations
a/photoelectron-spectroscopy

Lecture 6: The Atomic Orbital and Quantum Numbers

- Quantum numbers:
https://courses.lumenlearning.com/cheminter/chapter/quantum-numbers/

- The Schrodinger Equation and Particle in a Box (not tested):
http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/schr.html

- Quantum mechanics crash course:
https://www.youtube.com/watch?v=qO_W70VegbQ&list=PL8dPuuaLjXtN0ge7yDk_UA0ldZJdhwkoV&index=45

- Introduction to Quantum Mechanics by David J. Griffiths, available here or at your local MIT library:
https://www.cambridge.org/core/books/introduction-to-quantum-mechanics/990799CA07A83\

FC5312402AF6860311E

Lecture 7: Filling the Periodic Table and Our First Bond (it's Ionic)

- Electronic configurations:
https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Electronic_Structure_of_Atoms_and_Molecules/Electronic_Configurations/Electronic_Configurations_Intro

- Periodic trends:
https://opentextbc.ca/introductorychemistry/chapter/periodic-trends-2/

- Ionic bonds:
https://www.youtube.com/watch?v=zpaHPXVR8WU

Lecture 8: Ions, Ionization, and Valence

- Photoelectron Spectroscopy (PES):
https://www.khanacademy.org/science/chemistry/electronic-structure-of-atoms/electron-configurations
-jay-sal/a/photoelectron-spectroscopy

Lecture 9: Lewis Structures

- Drawing Lewis Dot Diagrams: Extra practice:
http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch01/ch1-3depth.html

- Video tutorial:
https://www.youtube.com/watch?v=ulyopnxjAZ8

3.091 Introduction to Solid-State Chemistry
Fall 2018