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5.112 Principles of Chemical Science, Fall 2005

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What I am going to do today is I am going to start talking about the development of atomic theory.

I am going to whiz through what the evidence is for the existence of atoms. And then we are going to talk about how the atom is not the most basic constituent of matter, how the atom can be divided into at least an electron and a nucleus.

And then what we are going to see is how the existing classical way of thinking, Newtonian mechanics cannot explain how that electron and that nucleus hangs together. And, later on in the course, we are going to see how that existing classical physics is not going to be able to explain how two atoms hang together.

We are going to look at the fundamental principles here of chemical bonding. I am going to get going on this subject. Then about three-quarters of the way through, I am going to stop. And then I will do some introductions of our teaching team this semester.

And then also we will talk about the mechanics of the course and some expectations of the course. Let's get going. Certainly, the Ancient Greeks were known to have pondered whether matter can be divided ad infinitum into smaller and smaller pieces, chopped up into smaller and smaller pieces, or whether there was a point at which you couldn't chop up matter any further.

Aristotle over here was one of those philosophers who believed that matter was infinitely divisible. You could chop it up ad infinitum. This is called the continuum theory of matter. It is a continuum.

There is no discreteness to matter. That was his view of the structure of matter, but there was a minority opinion. An opinion actually held by Democritus who was 100 years older than Aristotle. And Democritus believed that matter was composed of discrete particles called, in Greek, atomos, a meaning not, tomos meaning divisible, not divisible particles.

Well, for whatever reason, Aristotle's continuum theory of prevailed all the way up to the 17th century. And here he is depicted by Raphael, the frescos on the walls in the Vatican holding court on the continuum theory of matter.

But, at the same time that Raphael actually painted this picture, there were beginning to accumulate some observations about how matter behaved and how it reacted that did not quite jive with this continuum theory of matter.

And what were those observations? Well, one of those observations was by this gentleman, Robert Boyle. Guess what his profession was. Chemist? Good guess. He was actually a theologian, as most chemists were at that time.

You know him largely for the empirical observation that if you take the pressure times the volume of a gas it is always a constant. At least when the temperature is constant. But Robert Boyle also put forth probably the first idea of an element.

And he called elements certain primitive unmingled bodies. And he also put forth the idea that these unmingled bodies were the ingredients of perfectly mixed bodies. Just a pseudonym for molecules, for compounds.

And then there is the work of this gentleman, Joseph Priestley. Guess what his occupation was. Right, he was a priest. And what he did was he carried out some reactions of dephlogisticated air with various materials.

And what he found was that materials reacted more vigorously in dephlogisticated air than they did in undephlogisticated air. And, of course, dephlogisticated air is nothing other than oxygen. It is the air with the nitrogen removed from it.

But it really took this gentleman, Lavoisier, to understand what Priestley's experiments were all about. And what Lavoisier realized is that when materials were reacting with this dephlogisticated air, this dephlogisticated air was kind of adding to the material.

And he came to that conclusion because he did some very careful measurements of the mass of the dephlogisticated air plus the material before the reaction and some careful measurements after. And found that they were indeed equation.

There was a conservation of mass. And from that Lavoisier was really the first person to realize that a chemical reaction was analogous to an algebraic equation. He also went on to isolate 17 different metals and identified them as elements and nine different nonmetals and identified them as element.

But for all of his efforts, well, we all know what happened to him. He was advisor to the French Monarchy. The judge at his trial proclaimed the Republic has no use for Savants. LaGrange, who was a mathematician at that time, said, "It took about a moment to cut off that head, though 100 years will be required to produce another like it." Well, here we have some observations and we have -- Oh, I forgot one other person here.

That is this guy, J.L. Proust. J.L. Proust was also a French scientist at that time, but he was a little more politically savvy. And so he high-tailed it out of France and lived a long and productive life as a professor in Madrid.

And what he did were experiments. He recognized from the results that when two elements combine to form a given compound, they always did so in definite proportions by weight, regardless of what kind of method of preparation he used to make that particular compound.

Here is an example where matter didn't quite behave as a continuum. There was a discreteness of some sense to matter. And it really took John Dalton, an English schoolteacher with broad interests, to realize, or to recognize these observations of Priestley, of Lavoisier, of Proust that he could understand all of these observations if he resurrected the idea of Democritus, the idea of atomos, or atoms.

And so he forth some postulates. Well, those postulates are now known as Dalton's Atomic Theory, but they were postulates at the time. And those postulates say each element is composed of atoms, atoms of a given element are identical and that compounds form when atoms of more than one element combine.

And, of course, that atoms are not created or destroyed. And then, just an aside, Dalton, with his very broad range of interest, was also really the first person to document colorblindness in humans.

Colorblindness is also called Daltonism. You see, we are getting you set for medical school already. But I want you to recognize here that Dalton didn't actually do any of these experiments himself.

I think he could of, but he didn't. Instead he just said that if Lavoisier was right and Proust's observations are right, well, then I can understand those observations in terms of this framework of postulates.

And I point this out because this is a powerful method in science, a powerful way in which science works in that there are often some observations seemingly disparate. And then somebody comes along and recognizes a unifying factor.

In this case, the presence of atoms or discrete particles. Now, of course, Dalton's Atomic Theory here was not immediately accepted. And rightfully so. It needed further substantiation. And that further substantiation came in the form of work by this gentleman, Joseph Gay-Lussac, the Law of Combining Volumes.

It came in the form of work by Lorenzo Romano Amedeo Carlo Avogadro's hypothesis. And here I want you to realize that, even though you didn't know it, you indeed can read Italian. It says "equal volumes of gases under the same conditions of temperature yield the same number of molecules or atoms." There you go.

That is from an Italian stamp. You can read Italian. And that further substantiation came from the work of this gentleman, Ludwig Boltzmann, gas kinetic theory, who recognized in all the pressure of a gas that must be due to individual particles that are moving and that are ramming into the walls of some vessel.

That must be what gives rise to pressure. And then, finally, it took a statesman, Cannizzaro. And what Cannizzaro did was he got the scientific establishment at that time, and the scientific establishment at that time for sure was a small group of pale males, to listen to Dalton's Atomic Theory and to the supporting data from Avogadro and company.

And ultimately got them to say, yes, there is something to it here. And so by the late 1800s, the idea of atoms was pretty strongly engrained in the scientific community. Now, of course nowadays we can actually see individual atoms for molecules.

And so here is a picture of 28 individual CO molecules arranged in the form of a little man or a little woman, I don't know which. And each one of these CO molecules is an orange ball. And what you are looking at are these CO molecules bound to a platinum surface.

They are bound to a platinum surface such that the carbon end is down and the oxygen end is up. And there is a really good reason why the carbon end is down and the oxygen end is up. And Professor Cummins, whom I am going to introduce to you in a few minutes, is going to talk to you about what that really good reason is in the second half of the course.

We know why this is case. What you are looking at here is really looking at the oxygen end of the CO molecule, because we are looking at a top view. All right. How is this image made? Well, this image was made by a technique called scanning tunneling microscopy that was invented before you were born, I am sorry to say.

I am sorry for myself to say. It was worked on by Ruska and then perfected by Binnig and Rohrer. And they earned themselves a Nobel Prize for this work. And the way this techniques works is the following.

What you are going to do is take a thin tungsten wire. It might be 0.01 inches in diameter. And you etch it down to a fine tip. You stick it in some potassium hydroxide, do a little electrochemistry and etch it down to as fine a tip as you can make it.

Then you attach that tungsten wire to something called a piezoelectric crystal. And a piezoelectric material is one in which, if you put a voltage across it, you can make it expand a little bit, 10-20 angstroms or so.

And if you can make it expand a little bit like that, well, then you've got control on an angstrom-type level. You attach it to some piezoelectric crystal here then it allows you to move that tungsten tip by a very, very small amount.

You bring that tungsten tip close to the top of this CO molecule sitting on this platinum surface. And say you bring it to within, oh, I don't know, 5 angstroms or so from the oxygen atom. Now, the tungsten has electrons.

And since this is a bulk metal, some of those electrons are not firmly attached to a particular nuclei. There is a sea of electrons. And what we are going to do is put a negative potential on that tungsten tip.

And we are going to ground here this platinum surface. Now, these electrons on the tungsten, they are in this environment of a negative potential. And that is a high-energy state for them because they are negatively charged particles.

If I were to draw here an energy level diagram, I am going to represent then the energy level of the electrons here in this tungsten, around this tungsten tip as some high energy over here. There are electrons on the tungsten.

Whereas, the electrons associated with the platinum and the CO here, all of which are in contact with each other, well, they are at ground. That is a lower energy state for these negatively charged particles.

We are going to represent it by this. This is the electrons on platinum. And so this axis here is kind of a distance access. These are the electrons on the tip. These are the electrons on the platinum.

We are measuring kind of distance here, from here to here, in the vertical direction there. There is a thermodynamic driving force for the electrons on the tungsten tip to want to be here on the platinum, but the problem is that this tungsten is not in contact with this oxygen end here.

There is a gap. And if this is in a vacuum, we call this a vacuum gap. And so for an electron to be inside of this vacuum gap, well, that is a very high energy state for those electrons. And so, if we were to look at an energy level diagram here, that energy actually goes up pretty high before it comes back down.

There is a barrier to getting the electrons from the tip to the platinum surface. Well, you have seen this kind of reaction coordinate before. You have, I am sure. If you look at an energy level diagram here for some reactions, sometimes you have reactants here at a high energy and products here at a lower energy.

And, in order to get from reactants to products, there is a barrier, an activation energy barrier. You called it Eact or something like that. And you know that in chemical reactions typically what you have got

to do is put energy into the system in order to get over this barrier before you get any energy out, before the reaction can proceed.

And that is what happens in a lot of chemical reactions. There is a barrier and you have got to supply that energy to get over it before you can make the reaction go. But over here, in the case of electrons, those electrons don't act like atoms and molecules do, for the most part.

These electrons, what do they do? They ignore this barrier and tunnel right through the barrier, go right through that brick wall. How can they do that? Well, they can do that because they are quantum mechanical particles.

We cannot treat those electrons like we treat atoms and molecules which, for the most part, behave as classical particles. And, actually, this is going to be the subject of the first few lectures here, the need for this new kind of mechanics to explain phenomenon like this and to explain chemical bonding.

All right. So, these electrons tunnel right through. What does that mean? Well, what that means here, for this experiment, is that if I then take and attach a wire to the tungsten tip and a wire to the platinum surface and I put an ammeter in between, I will see a measurement of a current.

There are electrons going from this tungsten tip to this platinum surface. I measure a current. Well, that is nice. But now, from that, how do I get this image of these 28 CO molecules? Well, what I do is also have this tungsten tip mounted not only on a piezoelectric crystal that allows me to go up and down.

But another piezoelectric crystal which allows me to move it from side to side with control on the order of an angstrom. I can take the tungsten tip and I am going to move it over by a certain amount.

And exactly I am going to know that certain amount is because I calibrated my piezoelectric crystal. But now, when I move that tungsten tip over, what is going to happen to this current here? Pardon? It is going to go down.

It is going to plummet. It is going to go to zero. Why? Because when I move this tip over, I increase the distance between the end of the tip

and the oxygen onto the molecule. And when I increase the distance, what I do is make this barrier wider.

And the wider the barrier is, the more difficult it is for those electrons to tunnel through. And so the current actually goes down. To compensate for that, I am now going to take the tungsten tip and move it down by just enough such that I reestablish the current that I originally have.

And, of course, I know exactly by how much I moved it down because, again, I have my tip calibrator. I've got two points now. I need a third point. I am going to take that tungsten tip and I am going to move it over again.

Again, the current is going to go down. But, in order to reestablish the original current I had, I am going to move this down further. And, again, I will know how much I move the tip over and I will know exactly how much I move the tip down.

To get that image, I am going to provide a color code. I am going to say that when the tungsten tip is the largest distance away from the surface, well, then that is going to show up here on this picture and it is going to show up as a very light color.

That is the highest points. When the tungsten tip is a little bit closer to the surface, well, that is going to show up as the darker colors. And, as it gets lower and lower and lower, it is going to be deeper and deeper orangey.

Finally, when I am actually tunneling to the platinum surface, instead of a CO molecule, I am going to make that a blue color. That is how we get the image of this molecular man. Now, you do see that these CO molecules are in the form of a little person.

This does not represent, in the most [UNINTELLIGIBLE] language, intelligent design. Rather, this represents the work of a very patient experimentalist, i.e., graduate student, who spent 24 hours, and I know this to be the case, moving these CO molecules into this particular arrangement.

How did he do that? Well, how he did that is the following. What he did was took this platinum surface and then opened up a bottle of CO in the vacuum chamber, or let some CO into the vacuum chamber, and

the molecules just absorbed anywhere they wanted to, well, sort of anywhere they wanted to on this platinum surface.

First of all, he had to figure out where the molecules were. The soccer balls are the CO molecules and the tungsten tip here is my leg and my foot. And so the first thing he did was scan the surface in order to figure out where the CO molecules were and goes, OK, I know where they are.

Then he brought this tip down right next to one of the CO molecules. Then he gave that piezoelectric crystal a pulse of voltage which jerked it and the CO molecule went flying away. Well, that is nice, but now where is it? Again, you have got to go scan along the whole surface to find it.

Well, he pushed it over too far. Now we have got to come over here, put the tip down, give another voltage pulse before his tip breaks. Well, you get the idea. 24 hours later, you've got it. This is the beginnings of nanotechnology.

You can see that it is going to be a long time before manipulation of individual atoms and molecules like this, one at a time, before that competes effectively with synthesis in a beaker where you get the molecules right where you want them because of chemistry instead of this mechanical manipulation.

Well, even though 100 years ago these direct observations of atoms and molecules was not possible, it was by the late 1800s pretty well accepted, or the evidence for the atomic structure of atom, atoms as the most basic constituent of matter, was really pretty compelling.

And, in fact, by the late 1800s, it was basically believed that the theoretical structure of the universe was complete. Nature was understood. There were no big discoveries to be made yet. And, in fact, there was some justification for that attitude, because certainly by the late 1800s Newtonian mechanics, the mechanics that described how bodies all around us moved, including astronomical bodies, well, that had already been known for over 200 years.

Thermodynamics was formulated already by that time. Statistical mechanics was also formulated by that time. Statistical mechanics is a field that relates the microscopic description of matter to the macroscopic behavior of matter.

And, very importantly, there were experiments by Young, Fresnel and Hertz that seemed to put to rest the notion that light was a particle. Those experiments really nailed, or seemed to nail the idea of light as a wave, light has wavelike particles.

They verified Maxwell's equations that unified the fields of optics and electromagnetism. All of these accomplishments surely did justify a very proud feeling amongst the scientific community. And, at that time, the feeling was that the work that remained was largely to investigate the next decimal place and that is it.

Well, if you look really carefully, though, at the evidence, even with all of these accomplishments, there were beginning to be, in the late 1800s, some experiments that were suggesting that, one, maybe the atom was not the most basic constituent of matter.

That was the first set of measurements that indicated something was amiss, the fact that the atom wasn't the most elementary particle. And we are going to look at these sets of measurements. Second, the other observation that hinted that this classical thinking as amiss was the observation of the photoelectric effect.

Because the photoelectric effect, what it did was showed that light was behaving like a particle and not a wave, and that sent a lot of consternation throughout the scientific community. We are going to look at these two tracks.

And we are going to start by talking about the fact that the atom is not the most basic constituent to matter. That at least you can divide the atom up into an electron and a nucleus. We are going to start here with this gentleman J.J.

Thompson. Remember that name. It is going to come back. Discovery of the electron. This is 1987. What J.J. Thompson was interested in doing was understanding what a discharge was, or what made up a discharge.

For example, if you have a glass vessel that you evacuate and then you have a cathode in that glass vessel and you have an anode in that glass vessel, and you also put some molecular hydrogen in it, fill it up with molecular hydrogen.

But now what you do is put a negative voltage on the cathode and a positive voltage on the anode. And you crank up the potential energy difference, the voltage distance between the cathode and the anode.

And you keep cranking it up. You have to get really pretty high, but at some point all of a sudden what happens is that the gas here begins to blow. And you get the establishment of this discharge, this plasma.

And J.J. Thompson was just interested in finding out what was in this plasma. What he did to investigate it is he punched a hole in this anode right here and let out a little bit of this plasma. He let it impinge on a kind of phosphor screen here.

Even though the plasma leaking out was kind of glowing in the dark, well, it also was glowing when it hit the phosphor screen. That lit up. But then he took a pair of parallel metal plates above and below this luminous beam and put a potential difference on them, some delta V.

And this delta V is just a fraction of what this delta V is, so it is very small. But what he noticed is that some of this luminous beam was actually attracted toward that positively charged plate. And so, if you have got something that is attracted to this positively charged plate, what does it mean about this particle? It is negatively charged.

It is just Coulomb's interaction. And he could measure right here the amount of deflection from the center line. I am going to call that amount of deflection delta X subminus to indicate that this looks like a negatively charged particle.

Now, Thompson also knew enough electromagnetism at that time to realize that the amount of that deflection has to be directly proportional to the charge on that particle. In other words, the greater the charge the larger the deflection.

I am going to represent that charge by E subminus. He also recognized that the heavier that particle, the more difficult it is going to be to deflect the particle to the positively charged plate. That amount of deflection is going to be inversely proportional to the mass of that negatively charged particle.

But then Thompson did a further experiment. He increased delta V even more. And here I am taking a little liberty with the story. It is a little bit more complicated, but I am just trying to get the essence here across.

He cranked this up some more. And then, if you looked really, really carefully, what happened is he also saw some of this being deflected toward the negatively charged plate. Indicating that, low and behold, there must also be some positively charged particles in this luminous beam.

And he called that deflection delta X subplus. Again, the amount of deflection for the positively charged particles has to be proportional to the charge on that positively charged particle and inversely proportional to the mass of that positively charged particle.

But the other critical observation that he made was that the amount of deflection for a given voltage, for that negatively charged particle was much, much larger that the amount of deflection for the positively charged particle.

That is the evidence. Now we have to think. Now we have to make some guesses. What he guesses is that the positively charged particles here where H plus. How did he know that? Well, what he did know is that in this plasma there were some neutral hydrogen atoms.

He knew that. How he know that I am going to tell you, or we are going to talk about in a few days. But he knew that this plasma takes the H2 molecule and tears it apart and makes hydrogen atoms. And he knew it was neutral.

And so he reasoned that what must be happening is that something has to be coming off of this hydrogen atom to make it a positively charged particle. He said, OK, this is going to be H plus. But then, because this was neutral to begin with, whatever came off of the hydrogen has to be that negatively charged particle so that when they come together they are neutral, because a hydrogen atom is neutral.

And, of course, ultimately that negatively charged particle was called an electron. But the key point is that he said, well, it must be then, when these two particles come together, you are going to have a neutral particle.

It must be that the absolute magnitude of the charge on that negatively charged particle, the electron, that has to equal the magnitude of the charge on that positively charged particle, this hydrogen plus ion.

That was the conjecture. Well, if that is the case, if I then take a ratio of delta X minus the delta X plus, what I am going to get here is just that it will be equal to the mass of the hydrogen ion divided by the mass of this negatively charged particle, the electron.

But the observation here is that this deflection, for the negatively charged particle, is much larger than it was for the positively charged particle. That must mean, if this is an equality, that the mass of this hydrogen ion is much, much greater than the mass of this negatively charged particle, the electron.

And this is the stunning result. It is stunning because, at the time, it was already known that a hydrogen atom is the least massive atom. There wasn't evidence for any other atom less massive than a hydrogen atom.

And so here, in this experiment, what we are finding is that there is a particle that is less massive than the hydrogen atom. You can chop the hydrogen atom up. The atom is not the most basic constituent of matter.

There is some other particle here, which we are going to call an electron, that is less massive than a hydrogen atom. That was the first piece of evidence for being able to split that hydrogen atom, or that atom up into smaller particles.

The first evidence that the atom was not the most basic constituent of atom. Now, it took another ten years, the Millikan oil-drop experiment, for this ratio to actually be measured accurately and for the mass of the electron to actually be measured accurately.

And what we now know is that it takes 1,836 masses of the electron to equal the mass of a hydrogen atom.