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5.111 Principles of Chemical Science, Fall 2008
Transcript – Lecture 9

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PROFESSOR: OK. Let's get started. Can you go ahead and take 10 more seconds on this first clicker question here? OK. So it looks like most of you got that the electron configuration that we're writing here is for copper. So I'm actually going to give the benefit of the doubt that the people that didn't get it right were rushing to get out their clickers and didn't have time to think it all the way through. Remember that when we're talking about $4s^1, 3d^{10}$, that's one of those exceptions where a completely filled d orbital is more stable than we would expect. So, that's actually the electron configuration we have when we're talking about copper and some other exceptions in the periodic table that you're going to be looking at.

So, hopefully, if you were to go back and look you could see that this is, in fact, copper. We're actually going to do one more clicker question to get started with today, and as we do, I'll explain something we're going to be trying today, which is a little bit of a friendly competition in terms of answering the clicker questions correctly. So we've tagged each of your numbers to your actual recitation, so we can see today which recitation actually is going to be doing the best in terms of clicker questions, who's going to get the most correct today.

So, you may or may not know this about your TAs, but this is a pretty competitive group of TAs we have this year, and they like to brag about how smart their recitation is, how good questions they're getting in the recitation section. So, do your TA proud today and see if you can be part of the recitation that gets the most correct in terms of a percentage. And at the end of class we'll announce which recitation that is, we'll also make sure to give you a little bit of a prize if you are, in fact, in that recitation. So we have extra incentive to get these clicker questions right.

So, in this one we're selecting the correct electronic configuration for an ion. So, why don't you go ahead and take 10 more seconds on this second clicker question for our intro.

OK. So, it looks like we have a little bit of a mixed consensus here. Let's go over this question. And I know there's a lot to talk about about this competition, but let's just get into listening mode here and talk about how we can figure out what the correct electron configuration is for this ion. Remember, ions are a little bit different. The first thing we need to do is write the electron configuration for the atom itself, and then we need to take an electron away. So here we're talking about $v + 1$, so if we were to write it just for the neutral electron itself, we would find that the electron configuration is argon, that's the filled shell in front of it. Then $4s^2$ and $3d^3$. So this would be for the actual filled, the completely neutral atom.

But remember what we said, which was when we talked about, this is at the end of class on Friday, we said that it turns out that even though 3d is higher in energy when it's not filled, once we fill it with an electron, these 2 orbitals actually switch place in terms of energy. So if we were to write this in terms of energy, we would actually have to rewrite it has 3d³, and then 4s². So, which orbital would we take an electron out of if we were ionizing this atom here? The s. So, we would actually take an electron out of the s, which gives us 3d³ and then 4s¹.

So, it's a little bit of a trick when you're dealing with ions. The best suggestion is just to write it out completely for the neutral atom, and then you want to take an electron out of the highest orbital. It makes sense that it's going to come out of the highest occupied atomic orbital, because that's going to be the lowest amount of energy that's required to actually eject an electron.

All right. So let's go to today's notes. And actually before we start into today's topics, I want to remind everyone and hopefully you all do remember that our first exam is coming up and it's coming up in exactly a week, so it'll be a week from today, next Wednesday. And on Friday in class, at the beginning of class, I'll go over just in all the detail you could possibly imagine everything you need to know logistically for the exam -- where it is, what you do, what kind of calculators you can bring, which by the way are any calculator. So you'll get all of that information on Friday. So don't worry if you have some questions right now. I just want to let you know that.

The other thing I want to let you know is that instead of having a new problem-set that you'll be assigned this Friday, what we'll do instead is we'll give you some practice problems, and these will be just more of the same type of problems that you saw before but that's another chance to try them out more. These won't be graded, you don't have to turn them in, it's just to give you some extra practice if you want while you're studying for the exam.

We'll also post an exam from a previous year so you can actually see exactly what the format's going to look like. So when you go into the exam a week from today, it'll all look really familiar, you'll be comfortable with the format and you can just dive right in and start answering the questions. So you'll have all that information and we'll get it to you on Friday.

The other quick thing I want to say is that I do have office hours today from 3 to 5, so feel free to stop by if you have questions about problem-set 3 that you're finishing up. And also, for those of you that did sign up for the pizza forum tonight, that's going to be at 5 o'clock, it's in room 56-502, so we'll see some of you tonight for that as well.

All right. So, let's move on to what we're talking about today. What we're going to start with is discussing photoelectron spectroscopy, which is a spectroscopy technique that will give us some information about energy levels in multielectron atoms. We'll then take a turn to talking about the periodic table, we'll look at a bunch of periodic trends, including ionization energy, electron affinity, electronegativity and atomic radius. And then, if we have time at the end, we'll introduce one last topic, which is isoelectronic atoms and ions.

I also want to note that the end of the material today, so this last topic here, that's the end of the material that's going to be on this first exam. So whether we finish it today, or more likely when we finish it up on Friday, once we get passed

isoelectronic atoms, that's it, that's all you need to study for this first exam. So from that point on it'll be exam 2 material, so depending on how you like to come compartmentalize your information, you can separate that in your brain in terms of what you're trying to learn right now versus what you can put off until a little bit later.

So, let's start with talking about photoelectron spectroscopy. This actually relates very closely to what we discussed in class on Friday before the long weekend, and what we were talking about is the energy levels of multielectron atoms. So what we'll start with today is talking about the technique that's primarily used to actually experimentally figure out what these different energy levels are. And this is called photoelectron spectroscopy, and essentially what it is is very similar conceptually to what we were talking about way back in the first couple lectures when we were talking about the photoelectric effect.

Because here what we have is some atom that we're studying, in the case, it's going to be a gas, and we hit it with a photon that has some incident energy. So $e_{\text{sub } i}$, some energy that the photon comes in with, and if it has sufficient energy to eject an electron, it will do that, and our electron will be ejected with a certain kinetic energy, which is going to be whatever energy is left over from the initial energy we put in minus what was taken up in order to actually ionize or eject the electron.

So, you can see how this can directly give us different ionization energies for any atom that we're interested in studying. For example, with neon we can think about all of the different orbital energies we could be looking at. In the first case, so here is the electron configuration of neon. So we can think about what is our most loosely-bound electron, what's that highest energy orbital, and it's going to be the 2 p orbital, that's going to be what's highest in energy. So if we're going to eject an electron using a minimum amount of energy, that's where it's going to come from. So, you can imagine, that we'll actually probably have a lot of kinetic energy left over if we put a lot of energy in in the first place. We're only using up a little bit to eject the electron, then we'll have a lot left over.

So, one difference between photoelectron spectroscopy and, for example, the photoelectric effect is that in this case, we're not just looking at one energy level, which is what we were looking at from the surface of a metal, now we're talking about this gaseous atom. So we can actually pop an electron or eject an electron from any single orbital that is occupied within the atom. So, for example, it's not just the 2 p that we could actually take an electron from, we could also think about ejecting an electron from the 2 s orbital. Now this, of course, is going to take more energy because a 2 s is lower, it has a more negative binding energy than the 2 p, but that's OK as long as we put in enough energy, but what we're going to find is the kinetic energy coming out with the electron is actually going to be a little bit less, right, because we had to use up more energy to eject the electron, so we don't have as much left over.

There's actually one more orbital that we could talk about if we're talking about this sample case of neon, which is a 1 s orbital, and if we're talking about a 1 s orbital, now we're going to be even lower in energy still, so that means the minimum energy required to eject an electron is going to be at its highest, so that means the energy that we have left over that turns into kinetic energy for the electron, is now going to be really quite small.

And what happens when you irradiate one of these atoms that you're studying with this light is in photoelectron spectroscopy, you want to make sure that you put in enough energy to actually ionize any single electron that you have in the atom. So the way that we really make sure this is done is that we use x-rays. So you know that x-rays are higher frequency than UV light, for example, that means it's also higher energy than UV light, and if you think back to our photoelectric effect experiments, do you remember what type of light we were usually using for those? Does anyone remember?

Yeah. It was UV light that we used. Well, we can't guarantee with UV light we'll have enough energy to eject every single electron, so that's why when we use x-rays, they're higher energy, you can pretty much be guaranteed we're going to eject all of those electrons there.

So I said that this technique was used to experimentally determine what the different binding energies or the different ionization energies are for the different states in a multielectron atom. Another way to say states is to talk about different orbitals. So we can do this directly as long as we have certain types of information.

The first that we need to know the energy of the photon that's incident on our gaseous atom. The second piece of information we need to know is what actually the kinetic energy is of the ejected electron, and that's something we can just measure by measuring its velocity.

So we can use an equation to relate the incident energy and the kinetic energy to the ionization energy, or the energy that's required to eject an electron. This should all sound incredibly familiar, like I'm just repeating myself in terms of photoelectric effect, because essentially that's what I'm doing, and that's one reason we spent so much time and did so many problem-set problems on the photoelectric effect.

So what we're saying here is the incident energy, so the energy coming in, is just equal to the minimum energy that's required to eject an electron. When we talked about the photoelectric effect, that was called the work function. In this case, it's called the ionization energy, plus whatever kinetic energy we have left over in the electron. So if we want to solve for ionization energy, we can just rearrange this equation. Our ionization energy is going to be equal to the incident energy coming in, minus the kinetic energy of the electron.

So, let's take a look at the different kinetic energies that would be observed in a spectrum for neon where we had this incident energy here. And it turns out that the first kinetic energy that we would see or the highest kinetic energy, would be 12.32 electron volts. So if that's the case doing a quick little calculation, what would the ionization energy be for a 2p electron in neon?

Yup, 22. So, basically all we did was take 12.54, subtract 12.32, and we got 22 electron volts.

We can do the same thing for the other observed kinetic energy. So, for example, in the second case, we say that we see 12.06 in terms of the kinetic energy. Same sort of subtraction problem, what do we have for the ionization energy of the 2s electron?

Good, quick math. All right, so 48 electron volts. And let's look at the final kinetic energy that we'd observe in this spectrum, which is 384 electron volts, so what is that third corresponding ionization energy?

I couldn't quite hear, but I have a feeling everyone said 870 electron volts.

So, we can actually kind of visualize what we would see if we were looking at a photoelectron spectrum. And what we would see if we were graphing, for example, increasing kinetic energy, is we would see 1 line corresponding to each of these energies of electrons that we see coming out. And, of course, each of those electrons correspond to an electron coming out of a particular orbital. So in the case of 12.32, that is our highest kinetic energy, that means it's our lowest ionization energy -- it's the smallest amount of energy it takes to pop an electron out of that orbital. So that's why we see the 2p here, the 2s is 12.06, and it makes sense that what we see as the greatest ionization energy, which is also the smallest kinetic energy is that 1s orbital. Remember, because that 1s orbital is all the way down in terms of if we're thinking about an energy diagram, we're all the way down here, so we have a huge amount of energy we have to put into the system in order to eject an electron.

So what I want to point out when you're kind of looking at these numbers here, what the significance is, look at that huge difference between what the ionization energies are for what we call those valence electrons, those outer shell electrons, versus the ionization energy for the 1s orbital -- those are core electrons there.

So we can think about something I mentioned last time, which is when we're thinking about chemistry and what's really interesting in terms of chemical reactions, it's mostly valence electrons we're talking about, those are the ones that tend to be involved in chemical reactions. It makes a lot of sense when we look at it energetically, because if we think about a 1s core electron, that's going to be held really, really tightly to the nucleus. We see that we have to put this huge energy in to actually get a 1s electron ejected, so it makes a lot of sense that we wouldn't want to pay that energy cost in a normal chemical reaction. And we don't -- we very rarely would see these core electrons actually being involved in any type of a reaction.

All right, so one thing that I want to point out, which I said many, many times on Friday, and this is perhaps the last time I'll say it, but one last time is we can think about why we only see a line for the 2p orbital, versus we don't see separate lines for a 2p_x, a 2p_y, and a 2p_z. Remember, we need those three quantum numbers to completely describe the orbital. Why do we just see one for all the p's? And the reason is that the energy of the orbitals, depend on two quantum numbers, and that's quantum number *n*, and quantum number *l*. *m* does not actually have an effect, in this case, on the energy of the orbital. So that's why we're not seeing separate lines in this spectrum.

All right. So let's go ahead and try an example here in thinking about photoelectron spectroscopy. So, let's say we're looking at an element and we have an emission spectra, and we know that it has five distinct different kinetic energies in that spectrum. We might be asked, for example, to determine what all of the different elements could be that would produce a spectrum that gave us 5 different lines.

So the first thing that we want to do, if we're thinking about something like this, is just to determine exactly what orbitals are causing the five different lines that we're

seeing in the spectrum. So, if we're talking about five different orbitals and we're talking about a ground state atom, we know that we just need to start at the bottom and work our way out up. So, our first orbital that an electron must be coming from is the 1 s. What comes after that? 2 s. All right, then what? 2 p. After that? 3 s. Next? 3 p, and that's 1, 2, 3, 4 -- that gives us five different options, five different orbitals, five different energies right there. So, then all we need to do to determine which elements that corresponds to is take a look at our periodic table. So we want to look at any element that has a 3 p orbital filled, but that does not then go on and have a 4 s, because if it had the 4 s filled then we would actually see six lines in the spectrum.

So that is relevant for all of these atoms here, so we actually have several different possibilities. It could be aluminum, silicon, phosphorous, sulfur, chlorine or argon. Any one of these different elements could actually produce a photoelectron spectroscopy spectrum that has five distinct lines. If I went on and told you what the different incident light was, and what the electrons were ejected with, and then you could look up the ionization energy for the particular different elements, you should be able to actually determine exactly which element it is, but just with the information given, we can only narrow it down to these choices here.

So let's actually let you try another example of solving a problem that has to do with one of the spectrums. So, let's turn to another clicker question here. Remember, your answer holds great weight in terms of the state of the TA bragging for next week. So, how many distinct, so again, we're talking about distinct kinetic energies, would be displayed if you're talking about a spectrum for the element hafnium, and I'll tell you here that it has a z of 72, so you don't have to spend two minutes searching your periodic table. The period of table's on the back page of your notes if you don't see that there.

All right. It looks like a lot of you are done, so let's take 10 more seconds here. Part of the challenge is speed, too, how quickly you can get these answers in terms of getting them in on time. So let's see what we say. All right. So I think I can safely say that most people had the right idea and were counting quickly, though I have a feeling that some people who wrote 13 might have forgotten about those 4 f, the 4 f electrons. So, remember when you're looking at your periodic table, don't forget about the lanthanides, sometimes they come into play.

So it's actually 14, and the way that we got that answer was we just wrote out or just looked at your periodic table, figured out all of the different orbitals that you could have in terms of the principle quantum number, and then the l quantum number, and then write them all down -- it turns out to be 14, so that's what the answer is.

So, it looks like this is good, because we'll have some separation in terms of not everyone's going to get 100% in terms of recitations here, which is what we're going for.

All right. So let's turn our attention to a new topic, which is thinking a little bit about the periodic table, and also talking about periodic trends. And there's a lot we can explain by talking about what we see in the periodic table in terms of what different trends are in grouping different elements in different spots within the periodic table.

So, here we have a picture of Dmitri Mendeleev, who is one of the scientists responsible for first compiling the periodic table. You'll notice I have what's a very

flattering picture of him up here, and if you haven't done the reading yet you might not think this is particularly flattering, but if you look at the picture of him in the book, you'll notice I chose a very flattering picture of Dmitri up here, and here he's pondering putting these elements together in a periodic table. And he actually did this in the late 1800's, back before even all of the elements that we know today were discovered, really only about 60% or so, 70% were discovered then that we now know today. But still, he was able to put together a periodic table.

And what he did what he actually grouped things in terms of their chemical properties. So the way that we like to think of things now is in terms of electron configurations, right, but at the time that wasn't really understood. So, instead, it was amazing he was able to group things in terms of the properties that he saw. So, for example, if he was talking about the group one metals, lithium, sodium, potassium -- he noticed these were all very soft reactive metals, those were grouped together. Versus looking at, for example, helium or neon or argon, these are all inert gases, inert meaning essentially do not react, those were grouped together in the periodic table.

So basically, at the time he was just going on size and then traits, but what we actually know today is that we can also order things in the periodic table by electron configuration. In fact, that is the most logical way for us to look at it now. So, for example, if we're actually thinking about electron configuration and we look at lithium, sodium and potassium, these all have one valence electron. So basically, that means one electron in an s orbital in their outer-most most shell. So that explains why they're so reactive, they're all very willing to give up that 1 s orbital and then drop to a lower energy level.

In contrast, helium, neon, and argon all have filled shells. That also explains why they're very stable. They're not going to want to add on another electron, because then it'll have to jump a very large energy level and start filling in another shell -- go from n equals 2, to n equals 3, and n equals 4, and so on.

So it turns out that we can really know a lot just by looking at the periodic table. You will never in this class have to memorize anything about the periodic table. Depending on what kind of chemistry you go in to, you might accidentally memorize parts of the table, which is fine, but what you really want to know how to do is know how to use the periodic table. But you actually need to keep a few caveats in mind as you do this, which is the fact that trends predict a lot of chemical properties, but they can't predict everything in terms of biological properties. And after the periodic table was developed in the late 1800's, people didn't understand this quite as well, they took things a little more literally. They thought, for example, if you could do something with one element, if you looked at an element very close to it, it would be similar enough that you could maybe replace it with that.

Today we know, for example, if you can put one certain kind of element in your mouth or eat that, it doesn't necessarily mean you want to put the element next to it and your mouth as well, that might not be safe. But this is things we've learned as the years have gone past.

So, let's just take a quick example to show how not completely you can use these periodic trends, that there are limits. So if we consider lithium, potassium, and sodium, they're all together in the same group on the periodic table, knowing what we do about biology we can immediately think of sodium and potassium, or even just

knowing what you know about table salt, for example, that these are two elements that we find, and particularly in the ion form in very high concentrations in our body. For example, sodium in our blood plasma is almost to the point sometimes of 100 millimol or that's very, very concentrated. Similarly, we find it in table salt, we're taking it in all the time, the same with potassium, think of bananas, were always eating potassium. Not so with lithium. I don't think too many people and here are probably taking lithium. It turns out there's actually no natural function known in the body for lithium. So there's nothing naturally going on unless we were to introduce it ourselves in our body that we know of, at least, that involves lithium.

But this did not stop people, for example, in the late 1800's, early 1900's, and, in fact, in 1927 a new soft drink was put on to the market and they wanted to make a lemon-lime soft drink, these were very popular in the early 1900's, and to get sort of that lemony flavor, they decided to use citric acid, so that's a good idea, that gives that soury taste. And they wanted to use a soluble salt of citric acid, so they could have used sodium, they could have used potassium. But, you know why not do something a little special, little different, and they decided instead to use lithium. So, here we have this soda with lithium citrate, some of you might be familiar with this, soda is called 7-Up. So, 7-Up no longer has lithium in it, but from 1927 to 1950 it did, and, in fact, not only did they not try to hide the fact that there's lithium in the soda, this they used as a really special marketing technique, they really pointed out this is something that stands out about our soda, this is something special. There's a lot of good things about lithium. I don't know if you can see, probably not, what's written on here, so let me point out to you a few things.

Lithium, slenderizing, that's great to see in a soda. Other nice things about lithium in your soda, it dispells hangovers, takes the ouch out of grouch. That's very nice. So basically, you get a lot of benefit supposedly from this 7-Up soda from the 1920's or so. And this went on and was unregulated for some time, but at some point the Food and Drug Administration did take a step in, so here's a case where they did do something important -- that's not what I mean at all -- where they did take the step, they do many things that are important, often not quickly enough. Here's a -- actually here it did take 25 years, but they did, they did eventually step on before we started drinking 7-Up. And what they said was, look, you can't put this in, we're starting to notice it does some strange things. Because it was in the 1950's or so, maybe the late 1940's, that people started to discover lithium, even though it had no natural function, it did do something in our bodies. Does anyone know what was lithium's used for?

Yeah, it's an anti-psychotic drug, so, for example, some people with bipolar disorder even today still take it, it works really well for some people, for other people it doesn't work so well. But anyway, this isn't really something you want to have in your soda, so they did take it out eventually. Another side effect if you take too much lithium is death, so that's no good to have in sodas either, and it might not have been as big a deal back in the 1920's, but you can imagine with supersizing today, this might be a bigger problem.

So anyway, when we talk about periodic trends, it doesn't always match up. This was eventually taken out, and actually just for your interest, there was no overlap between the time when cocaine was in Coca Cola and lithium was in 7-Up, so there was a few years difference between those two times, but it's amazing to think about what does go into processed foods.

And the other thing to point out, which I don't know if this is true or not, but does anyone know -- well that's part's true, does anyone know what the atomic mass of lithium is? Yes, it's 7. So, I don't know if this is true or not, but I wonder if that's where the actual name 7-Up came from. So, even though we don't have the lithium anymore, we still keep that atomic number 7 around.

All right. So that is an anti-example of using periodic trends. So let's go to some actual real examples, which might come more in handy for this class. So it's going to keep in mind the limitations, so let's start off with talking about ionization energy.

Now this is a good place to start, because we are very familiar with ionization energy, we've been talking about it in a lot of different forms for quite a while -- it's that minimum energy required to remove an electron from an atom. And specifically, when we talk about ionization energy, it's assumed that what we mean is actually the first ionization energy. So, you can imagine, we could talk about any of the different electrons, or we could talk about taking out an electron and taking out second electron. Whenever you hear the term ionization energy, make sure you keep in mind that unless we say otherwise, we're talking about that first ionization energy. And we know what that's equal to, this is something we've been over and over, ionization energy is simply equal to the negative of the binding energy. So negative e , which is $\text{sub } n \text{ l}$, because it's a function of n and l in terms of quantum numbers.

So, let's think about kind of differentiating, however, between first ionization energy or just ionization energy, and other types such as second or third ionization energy, and let's take boron as an example here.

So, if we want to think about what the first ionization energy is of boron, what you want to do is write out the electron configuration, because then you can think about where it is that the electron's coming out of. The electron's going to come out of that highest occupied atomic orbital, that one that's the highest in energy, because that's going to be the at least amount of energy it needs to eject something. So what we'll end up with is boron plus, $1s^2, 2s^2$, and what we say is the delta energy or the change in energy as the same thing as saying the energy of the products minus the energy of our reactant here, and we just call that the ionization energy -- that's how much energy we have to put into the system to eject an electron. And again, this is just the negative, the binding energy, when we're talking about the $2p$ orbital.

So, this is first ionization energy, let's think about second ionization energy. So, second ionization energy simply means you've already taken one electron out, now how much energy does it take for you to take a second electron out. So in the case of boron here, what we're starting with is the ion, boron $1s^2, 2s^2$, and now we're going to pull one more electron out. The highest occupied orbital is now the $2s$ orbital, so we're going to end up with boron 2 plus $1s^2, 2s^1$, plus the electron coming out of there. And what we say when we talk about the delta energy is that this is going to be equal to $i e 2$, or the second ionization energy, or we could say the negative of the binding energy of a $2s$ electron in b plus. so it's important to note that it's not in b , now we're talking about b plus, because we've already taken an electron out here.

So, similarly if we start talking about our third ionization energy, this is going to be going from b plus 2, to $1s^2, 2s^1$. Now we're going to pull that second electron out of the $2s$, so we end up with boron plus 3, and then the configuration is just $1s^2$, plus our extra electron here.

So, what we call this is the third ionization energy, or the negative of the binding energy, again of the 2 s orbital, but now it's in boron plus 2 to we're starting with.

So, this raises kind of an interesting question in terms of what the difference is between these two cases, and we're talking about numbers of energy. So let's address this by considering another example, which should clarify what the difference is between these ionization energies. So let's think about the energy required now to remove a 2 s electron, let's say we're removing it from boron plus 1 versus neutral boron.

So, in the case of boron plus 1, what we are starting with is the ion, so we're starting with a 2 s electron, and then we're going to 2 s 1 here. And what we call the binding energy is negative 2 s in b plus -- this is what we saw on the last slide. And the second case here looks a lot more like what we saw when we were talking about photoelectron spectroscopy, because here we want to remove a 2 s electron, but it's actually not the highest occupied orbital, so that's not the one that would naturally come out first, but let's say we're hitting it with high energy light sufficient to knock out all the different electrons, and one that we end up knocking out is this 2 s here. So if we think about what that delta energy is, we call that the ionization of the 2 s, that's different from saying second ionization energy. And that's going to be equal to the negative the binding energy of 2 s in b, in neutral boron.

So, my question to you is are these two energies equal? No. All right, good answer.

So, we can think about why is it that these are not equal. In both cases we're taking an electron out of the 2 s orbital. And it turns out that if we're talking about a 2 s orbital in an ion, that means it doesn't have as many electrons in it, so what we're going to see is less shielding. There are fewer electrons around to shield some of that nuclear charge. So what we're going to see is less shielding, which means that it will actually feel a higher z effective.

So even though they're both 2 s electrons, in one case it's going to think its feeling more pull from the nucleus, and it, in fact, will be, than in the other case, and if its feeling a higher z effective, then it's actually going to require more energy to remove that electron, right, it's being pulled in closer and more tightly to the nucleus, you have to put in more energy to rip it away from that very close interaction.

So, that's the difference in thinking about different types of ionization energy, so it can get a little bit confusing with terminology if you're just looking at something quickly, so make sure you look really carefully about what we're discussing here. If you see a problem that asks you, for example, the third ionization energy versus taking a second electron out of the 2 s in a photoelectron spectroscopy experiment, those are two very different things.

So, let's make sure everyone kind of has this down, let's do another clicker question here. And in this case we're going to look at silicon, and we'll say if you can point out to me which requires the least amount of energy. So, which has the smallest energy that you have to put in in order to eject this electron? Will it be if you take a 3 s electron from neutral silicon, if you take a 3 p electron from the neutral atom, or if you take a 3 p from the ion? So this you should be able to know pretty quickly, so let's just take 10 seconds here.

All right, great. So most of you see that, in fact, the energy that's going to be the least that we need to put in is in case 2 here. Let's compare case 2 and 3, since this where some people seem to have gotten confused. In case 2, we're taking it out of -- oh, it's kind of hard to compare case 2 and 3 when we can't see it anymore. In case 2, we're taking the 3 p out of the neutral atom, whereas in case 3, we're taking it out of the ion. Remember in the ion, we're going to have less electrons around to counteract the pull from the nucleus. So we're going to feel a higher z effective in the case of the ion compared to the neutral atom. If we have a higher z effective, it's pulled in tighter, we have to put in more energy in order to eject an electron, so it turns out that that's why case 2 is actually the lowest energy that we need to put in. The z effective is lower, so we have to put less energy in to get an ion out.

So, let's take a look at this in terms of periodic trends -- that's our topic here, we're talking about periodic trends. So as we go across the row, and this is my beautiful picture of a periodic table here. As we go across the row what happens is that the ionization energy actually increases, and we can think about logically why it is that that's happening.

As we go across the row, what we have happening is that the z or the atomic charge -- I'm not talking about z effective here, I'm just talking about z -- the z is increasing as we go across a row, that's easy to see. But we're still in the same shell, so we still have the same n value as we go all the way across a row in the periodic table. So, in general what we're going to see is that what happens to z effective if we have z increasing but we're in the same shell here. Would it increase or decrease z effective?

All right. Kind of mixed thoughts here. So it turns out that it increases, and the reason is because the predominant thing that's going on here is that z is increasing. So the z is increasing, and what goes along with it is that the z effective is increasing, because it turns out that while we're in the same n , even though we know that energy depends on both the n and the l in terms of quantum numbers, while we're in the same n , the distance from the nucleus, it's pretty close, it's not hugely different. So the factor that predominates is that we're actually increasing z . That's why we see z effective increase, and that's why we see ionization energy increase.

As we go down a column, what happens is that the ionization energy decreases. We can also think about this in terms of z effective. This is because even though z , the atomic number is still increasing, we are also getting further away from the nucleus. So, remember when we talk about Coulomb force, what's holding the nucleus and the electron together, there's 2 things we need to think about. The first is this the z effective, or how much charge is actually in the nucleus that's felt, or the I guess we would say the z , how much the charge is on the nucleus that holds it close together. But the second factor is how far away we are from the nucleus. So, if we're really close to the nucleus, that's when z effective is high, but if we get really far away, then z effective is going to get low, because even though we have the same charge in the nucleus, the z effective gets lower.

So this is not even thinking about the other electron shielding, just if we think of the fact, all we need to think about is that the effect of going to a further away n actually dominates as we go down the table. We're getting further away from the nucleus because we're jumping, for example, from the n equals 2 to the n equals 3 shell, or from the n equals 3 to the n equals 4 shell. And when you're switching n 's, you're

actually getting quite a bit farther away. That's why in the earlier models of the atom, they're not horrible to sometimes think about just each n value as a little ring around. It's not complete and it's not accurate, but it's OK to kind of think of it in terms of how far we're getting away from the nucleus. So, as we go down a column, we see ionization energy's going to decrease.

So, this means we have the general trends down, so we should be able to look at actual atoms in our periodic table and graph them and see that they match up with our trends. So here we have that graphed here, we have atomic number z graphed against ionization energy, so, let's fill in what the actual atoms are here, and we can see in general, yes, we're following the trend. For row one, we're increasing, as we should, across the row. Let's look at row two also. Well, we're generally increasing here, we'll talk about that more in a minute. And also in a row three, yeah, we're generally increasing, there's some glitches here, but the general trend holds true.

Similarly we see as we go down the table, so as we're going from one row to the next row, so, for example, between helium and lithium, we see a drop; the same with neon to sodium, we see a drop here.

So it looks like we're generally following our trend, that's a good thing. But hopefully, you will not be satisfied to just make a general statement here when we do have these glitches. So you can see, for example, we have several places where instead of going up as we go across the row, we actually go down in ionization energy a little bit. So between b e, and b, between n and o, magnesium and aluminum, and then phosphorous and sulfur, what we see here is that we're kind of going down, or quite specifically, we are going down.

So, let's take a look at one of these rows in more detail to think about why this might be happening, and it turns out the reason that these glitches occur are because the sub shell structure predominates in certain instances, and that's where these glitches take place. So I've sort of just spread out what we have as the second row here, graphed against the ionization energy. So, let's consider specifically where these glitches are taking place.

So, let's look at the first one between beryllium and boron here. And the glitch that doesn't make sense just through periodic trends, is that it turns out that the ionization energy of boron is actually less than the ionization energy up beryllium. So I put the electron configurations and actually drew it on an energy diagram here, so we can actually think about why this might be happening.

So what is this, which element did I chart here? Which one is that, the boron or the beryllium? I couldn't tell what you said, sorry. So, I'm going to assume that was beryllium, and then it turns out that if that's beryllium, the other one must be boron.

So, we have beryllium in the first case here, it has four electrons, that's how we know it's beryllium, boron has five electrons. So, just looking at putting in the electrons, filling up the energy diagram here, we should be able to see a little bit why this is happening. And the reason is simply because the energy that we gain in terms of moving up in z , so from going to z equals 4 to z equals 5, is actually outweighed by the energy it takes to go into this new shell, to go into this new sub shell. So to jump from the 2 s to the 2 p, takes more energy than we can actually compensate with by increasing the pull from the nucleus.

So, it turns out that in this case, and any time that we see we're going from a 2 s to 2 p, filling in of electrons, we actually see that little bit of glitch in ionization energy. So it's shown here for the second row, but it's actually also going to be true for the third row. The same thing when you're going from filling in the 2 s to putting that first electron into the 2 p.

So that explains one of our glitches here, but we have another glitch, and that second glitch comes between nitrogen and oxygen. So, these sound more different, so I think I'll be able to distinguish. Which element is shown here? Yeah, nitrogen. So, nitrogen is shown here, we know that because it has 7 electrons. In this case, we're talking about 8 electrons, which is oxygen. So if we're comparing the difference between these 2 now, what you'll notice is that in nitrogen we have all half-filled 2 p orbitals, and now, once we move into oxygen, we actually have to add 1 more electron into 1 of the 2 p orbitals. There's no more 2 p orbitals to put it into, so we're going to actually have to double up. So now we're putting 2 electrons into the same p orbital, that's not a problem, we can do it, it's not a huge energy cost to do that. But actually there is a little bit of an energy cost into doubling up into a single orbital, because, of course, it takes energy when you create more electron repulsion, that's not something we want to do, but we have to do it here, and it turns out that that effect predominates over, again, the energy that we gain by increasing the atomic number by one.

So, our two glitches we see when we go from the 2 p, or from 2 s to start filling the 2 p, and then we also get another glitch when we've half-filled the 2 p, and now we're adding and having to double up in one of those p orbitals. Again, we see the same effect as we go into different rows as well.

So let's talk about another periodic trend, this one is called electron affinity. Electron affinity is actually the ability of an atom, or we could also talk about an ion to gain electrons. So it's the affinity it has for electrons, it's how much it likes to get an electron. We can write out what it is for any certain atom or ion x, so it's just x plus an electron gives us x minus. We have the minus because we're adding a negative charge from the electron.

So, basically any time we have a really high positive number of electron affinity, it means that that atom or ion really wants to gain another electron, and it will be very stable and happy if it does so. So let's look at an example of chlorine here.

So chlorine, if we talk about it in terms of electron affinity, we would be writing that we're actually gaining an electron here, and getting the ion, Cl^- . And the change in energy for this reaction is negative 349 kilojoules per mole. So if we have a negative change in energy for any reaction as it's written, what that actually means is we're giving off energy as the reaction proceeds. So, in other words, this Cl^- is actually lower in energy than the reactants were. So that's why we're giving off extra energy. We saw a similar thing as we saw electrons move from different levels. We can think of it in the same type of way when we're talking about actual reactions happening.

So, if we have energy that's released, would you say that the chlorine ion is more or less stable than the chlorine atom? Who thinks it's more stable, show of hands? All right, who thinks it's less stable? Very good. So it turns out it is, in fact, more stable. It's more stable because you actually -- this happens spontaneously, you actually get energy out of the reaction as this happens. And we haven't talked about reactions at

all yet, so you don't need to worry about the specifics of that exactly, but just that if you have this negative change in energy, you have a more stable product than you do reactant.

So, we were talking, however, about energy in terms of electron affinity, so we can actually relate electron affinity to any reaction by saying if we have this reaction written as here where we're gaining an electron, we say that electron affinity is just equal to the negative of that change in energy.

So, for example, for the chlorine case, we would say that the electron affinity for chlorine is actually positive 349 kilojoules per mole. That's a very large number, it's all relative, so you don't necessarily know it's large without me telling you or giving you other ions to compare to, but chlorine does have a very large affinity, meaning it's really likes getting an electron and becoming a chlorine ion.

One major difference between electron affinity and ionization energy is that when we talked about ionization energy, remember ionization energy always has to be positive. We will never have a case where ionization energy is negative. Electron affinity, however, can be either negative or it can be positive. So let's look at a case where it's actually going to be negative.

So, if we took the case of nitrogen, if we add an electron to nitrogen and go to n minus, we find that the change in energy is 7 kilojoules per mole. This means in order to do that we actually have to put 7 kilojoules per mole of energy into the reaction to make it happen. So this is not going to be a favorable process, we're going to find that the electron affinity is actually a negative 7 kilojoules per mole for nitrogen. So this means nitrogen has low electron affinity, it doesn't actually want to gain an electron. So, that also tells us that the n minus ion is less stable than the neutral atom itself.

So, we can think about trends in electron affinity just like we did for ionization energy, and what we see is a similar trend. Electron affinity increases as we go across a row in the periodic table, and it decreases as we go down a column. I left out the noble gases here because they do something a little bit special, and actually, I'm going to give you one last clicker question today to see if you can tell me what you think noble gases do. To answer this question you just really want to think about what does electron affinity means. It means how much a certain atom actually wants to get an electron. So do you think noble gases would have a high positive electron affinity, a low positive, or negative electron affinity? So, let's take 10 seconds on that.

All right. Great. So most of you recognize, if we switch back to the notes, that they do have a negative electron affinity. This should make sense to you, because they don't, in fact, want to gain another electron, because that would mean that electron would have to go into a new value of n , a new shell, and that's really going to increase the energy of the system. So they'd much rather just stay the way they are and not have another electron come on, and it turns out that halogens have the highest electron affinities.