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Transcript – Lecture 20

I am going to start now by telling you a little bit more about Lewis theory. Last time we went through aspects of the cube theory of Lewis and showed how that could account for single bonds and double bonds, but not triple bonds. And that when that was superseded by the electron pair theory, the idea being that these electron pairs would, in fact, be oriented at the vertices of a tetrahedron.

And I showed you that tetrahedron, as described in a cube last time, that you could then account for triple bonds. And, if you looked at the notes, you also saw that certain aspects of the dynamic behavior of certain bond types, rotation around single bonds, hindered restricted rotation around double bonds, and so forth. Those were accounted for by this electron pair theory in which the four pairs of electrons were oriented at these vertices of a tetrahedron.

So, that was another quite important triumph of that part of Lewis's theory. And the problem was, although that electron pair theory initially put forward by Lewis was so successful at accounting for the properties of many different kinds of molecules and was a good description of their electronic structure, there was one class of molecules, a very important class of molecules, namely those known as aromatic.

And the most important member of the class of aromatic compounds is, in fact, the benzene molecule. Benzene has the formula C_6H_6 . And we can easily calculate the number of valence electrons in benzene if we just say 4 for carbon times 6, plus 1 times 6 for the number of valence electrons from each of the six hydrogens. And that is 30 electrons. So, in trying to understand how these 30 electrons in a valence shell of benzene hold this molecule together, it is known to be a planar molecule, how do those electrons not only hold it together, --

-- but how do they account for the structure of benzene, and how do they account for its amazing stability? And this picture that I have drawn here is a representation of benzene, I will explain to you in a moment, but it comes from a person by the name of Ernest C. Crocker. Ernest C. Crocker was an MIT Bachelor of Science degree

holder, who earned that degree in 1917. He was an MIT undergraduate like you.

And he published a paper. Let me write down the reference for that paper. This is the Journal of the American Chemical Society, 1922, Volume 44, Page 1618. That paper was the first paper in which the Lewis electron pair theory was applied to an understanding of the electronic structure of aromatic molecules, in particular, benzene. And the amazing thing about that paper is -- Well, there are many amazing things, but one of the amazing things about that paper is that there is only one author on that paper, Ernest C. Crocker. And Ernest, who was a very bright individual, nonetheless did not go on in graduate school to earn a Ph.D. in chemistry, had many various chemistry-related interests. He explained the chemistry of many different kinds of fragrances and odors. I think he was referred to as "the man with the million dollar nose."

So, this person had quite a variety of interests. He worked in what was then the Applied Chemistry Laboratory at MIT after his graduation with his Bachelor of Science degree. And one of the things he was thinking about was how to use modern electronic structure descriptions, such as Lewis theory, to explain molecules like benzene. And so, if you go and read this paper, you are going to find a very lucid discussion of how the Lewis electron pair theory could represent benzene according to this formula that I have drawn here. And in this formula, there is considered to be an electron pair between each carbon and each of the hydrogen nuclei. There is an electron pair along each carbon-carbon axis, as shown here, and here, and so on, all the way around the ring.

And then, finally, you have six more electrons to come up to the number of 30, which is the number of electrons in benzene. And so, the question really is what to do with this remaining six electrons. And I have shown them around the outside of the ring, here, which is where Ernest arranged them in his work. And I just want to point out that he put forward the idea that these six electrons were circulating around the plane of the ring and involved a net one-half bond between each pair of adjacent carbon atoms in the benzene ring.

So, in effect, when we draw benzene this way, with a circle in the middle, we know that that circle represents the circulating six electrons in what we are going to call the pi system. But Ernest C. Crocker was the man who put the circle into the middle of benzene. And he was an MIT undergrad. And this was a sole-authored paper. Aromaticity has a vast history in chemistry, and it is still a very active

and unfolding history because of the problems, to our understanding, posed by electrons that seem to be circulating around a whole molecule rather than localized between pairs of nuclei.

So, Ernest Crocker, Bachelor of Science, 1917, MIT, had a huge hand in that. I thought you might find that interesting. And, having looked at benzene rings like that, I will now draw them perhaps another way that is also useful, which comes from Kekule. Because I want to continue our discussion of Lewis acid-base theory. And I am going to draw two molecules here that are going to be pretty similar.

When I write a molecule, as I have done here on the left, I haven't explicitly indicated each of the hydrogens that are present on the periphery of this substituted benzene ring. But you should understand from a formula like this that this is the molecule boron C 18 H 15. And over here I am drawing explicitly, at each of these peripheral positions on the substituted benzene rings, fluorine atoms in place of the hydrogens. So, this is a different molecule with formula B C 18 F 15. These are both Lewis acids.

And based on our discussion, last time, if you were to add ammonia to one of these molecules, where would the lone pair of electrons on the ammonia bind? The boron. So, yes, you have here a trigonal planer boron center. And, if you were to add an ammonia molecule, the lone pair of electrons would come in and stick to the boron -- -- because the boron is electron deficient. Just like the aluminum we discussed last time, it has only six electrons around it, and it wants eight. But what if we were to add one ammonia molecule to a flask containing both of those Lewis acids that would then be competing for the ammonia molecule?

What I am asking you to do is something I will ask you to do throughout this semester, and that is to analyze a molecule's properties based on its structure and its composition. Exactly. She said that it would preferentially stick to the one with the fluorines because these very electronegative fluorines are drawing electron density away from the boron. This is one of our most electronegative elements.

So you have a whole bunch of fluorines in that molecule. The whole thing, we call it perfluorinated. It is a perfluorinated triaryl boron reagent. These, in fact, are great Lewis acids, really powerful Lewis acids. And they are modern Lewis acids whose implementation in chemical processes has come about really in the last 10, 15 years. And, in fact we were talking a little bit about Professor Schrock last

time. In some of his research, he has used that perfluorinated Lewis acid as an activator in catalysis to get catalytic polymerization reactions to work. And that is a very popular approach these days in Lewis acid chemistry.

The design of new kinds of Lewis acids with interesting molecular architectures is something that is very much a current topic of interest in research in chemistry, because you can make lots of chemical processes happen when you have something that can tug on electron pairs. And this one tugs a lot harder than that one because this one has very electronegative fluorines to pull electron density away from that boron and to adjust the distribution of the electron density in the molecule.

And we will be talking more about electron density and distribution in a few minutes in connection with what I am going to show you now. And that is -- That has to do with this molecule, which is the SO two molecule. Anyone know where SO two comes from in nature? Or in the environment, I should say? Volcanoes, absolutely. And also coal-burning power plants. Coal is a very dirty fuel, and it contains a lot of sulfur. And, when you burn that coal without controlling the way you burn it, you emit SO two into the atmosphere.

So, that can be a big problem. And we will try to understand why. One of the things that SO two can do when it gets into the atmosphere is it can react with dioxygen. And that can give you -- -- SO three . And if SO two and SO three are present in the atmosphere and if there is also water present in the atmosphere, acid rain, that is exactly the type of process that we will be talking about here. SO two and SO three are examples of what we call anhydrides.

Anhydride is a word that means without water. And so you should not be surprised that SO two can react with water. And when it reacts with water, it takes up water. And the product of that reaction will look like this. I draw it like that. Okay. So, H two O plus SO two going to H two SO three. The name of this molecule is sulfurous acid. And, alternatively, when SO three reacts with water --

I have one extra electron pair that should not have been there. So, both SO two and SO three , as they react with water, are going from a situation in which they are electron deficient to a situation in which the sulfur attains an octet. Okay? And you should verify that the number of electrons that I have drawn up here actually is consistent with the elements that I am using with the stated charge that I am

using. But when SO_3 reacts with H_2O to give H_2SO_4 , we have now got sulfuric acid.

Okay. And, as I did over there, I have two acids that I want here now to compare in terms of their relative strengths. Here I have a Lewis acid SO_3 and a Lewis acid SO_2 engaging in a hydration reaction, which produces sulfurous acid and sulfuric acid. And the type of acids that these are on the bottom is Bronsted acids, -- -- distinguished from Lewis acids in that the way that they behave as acids is through ionization that produces a proton.

They are also Lewis acids because the Lewis definition of acidity is far more general, in saying that acids are simply entities that can accept a pair of electrons. Protons can accept a pair of electrons, so they are Lewis acids. But if you are talking about Bronsted acids, you are talking exclusively about protons that are produced by ionization of some kind of a Bronsted acid. Which one of these is the stronger acid? Sulfuric acid. And why?

Yes, down here. You got the other one right. Exactly. When this ionizes, you get SO_4^{2-} . I will draw it a slightly different way that is quicker. You get HSO_4^- . There is your ionization. And the idea now is that this O^- that you have, the negative charge can actually be shared among a greater number of electronegative oxygens here, namely four, as compared to here, where we have only three electronegative oxygens.

It is a consideration of the very electronegative elements in your molecule that will help you understand the properties that these molecules will have in terms of acid-base chemistry. Now, how many electrons do we have in the valence shell of SO_3 ? 24. And, that being the case, what molecule from last time does that remind you of? Maybe seeing a picture of it will help refresh your memory. AlCl_3 .

Exactly. I am going to show it to you anyway. And this is going to be faster than the last time, if I set this up right. Just to remind you. And if we could have the lights down just a little bit for a moment. I want to refresh your memory of the electron density distribution here in AlCl_3 . This is an electron density isosurface of AlCl_3 . And what you are noticing is that the electron density drops to a low value in between the central aluminum and the radially disposed chlorides, the three chlorides that surround that central aluminum ion. And the coloring in this is such that the blue regions represent regions in space where there is a high probability of finding paired electrons.

So, basically you have three Cl minus's that are packed tightly around an Al three plus. This is a very ionic compound. See the empty region in space between aluminum and chloride, and the polarization of that otherwise spherical cloud of electrons around the chloride in the direction of that positively charged aluminum? There is your electron density distribution for that. And now I want you to keep that in mind, and we will compare the isoelectronic SO three molecule to it.

SO three . Here is another case where we have 3 times 8, 24 valence electrons in a system. But the character of this molecule in terms of electron density distribution is very different. While on the blackboard, I am not able to really tell you very much about the difference between SO three and AlCl three, here I think you can see that indeed they are quite different. This is an electron density isosurface at the same contour level as what we were looking at for AlCl three.

Now, to explain this and to understand just what is going on here, you need to remember that the electronegativity difference between the central sulfur and the peripheral oxygens is not very great compared to the electronegativity difference between aluminum, which is a very electropositive and metallic element, and chlorine, which is a very electronegative halogen. And so, what that results in, as shown here, is a much more equal sharing of the electrons between that central sulfur and these peripheral oxygens. So, even though these things are both Lewis acids and they both have 24 valence electrons, the electron density distribution in three-dimensional space for these molecules and the covalent versus ionic character of these molecules, is really quite different.

Our section that is going to be devoted to bonding has not really kicked into gear yet, but the nice thing is that Lewis theory applies both to acid-base chemistry and to bonding, so we are able to talk a little bit about that. In a few moments, I will tell you a little more about an issue that is very important in chemistry as regards bonding. And it has to do with what happens when acids, like sulfuric acid, ionize in water. When Bronsted acids ionize in water, we get this ion produced. H three O plus, which is the hydronium ion.

That is to say that if you ionize in water some Bronsted acid, the protons that are produced through that ionization are not floating around freely, naturally, because they are positively charged and they are attracted to negatively charged electrons. So, they look around in solution and find the next source of an electron that they can. And you

know that if we draw out a molecule like water, according to the Lewis dot structure, it has two extra pairs of electrons, in addition to those two pairs of electrons it is using in making bonds to the two hydrogens that are on the oxygen of the water molecule. So, H plus is not just isolated around by itself in solution.

It perches on an oxygen lone pair. So, H three O plus is what you get when Bronsted acids ionize in water. And furthermore, when you put these things in solution you find that you organize the water molecules that are close to the hydronium ion. Let's draw here a neighboring water molecule. And another one. And I think you can imagine that throughout a solution, we might have many of the kinds of interactions that I have drawn here as dotted peach-colored lines. Those lines represent what we call hydrogen bonds. And hydrogen bonds are enormously important in chemistry.

Later, when we talk about the structure of proteins in DNA, in particular, you may be aware that the DNA double helix is held together by a network of hydrogen bonds between complimentary base pairs. So hydrogen bonds are not only restricted to the hydronium ion in aqueous solution. There are many other types of molecules that can form what we call hydrogen bonds. Another really interesting thing is that in water, the hydronium ion can move around really rapidly, much more rapidly than molecules normally diffuse through aqueous solution. And the reason for that is if you look at the arrangement of electrons and nuclei here, all I have to do is, without even moving the nuclei much at all, reorganize the hydrogen bonding network as such.

And now you can see that through just a slight set of motions, our hydronium ion has moved from the left-hand side of this hydrogen bonded network, where you can see that it is indicated with the positive charge and the three solid lines drawn to the oxygen, over to the right-hand side. But it did that not by coming off and moving over, but rather through just redistribution of the electron density, so that the positively charged part ends up down on the other side. And so this way of propagating hydronium ions in aqueous solution is one of the really special aspects of Bronsted acid chemistry that takes place in water.

And I think I will also show you what a hydrogen bond looks like from the standpoint of electron density. First, I am just going to show you the position of the nuclei in a very simple hydrogen bonded system. Here what you can see, the oxygens are drawn in red as spheres and

the hydrogens are drawn in white as spheres. You can see that the geometry around the oxygen atoms is slightly pyramidal. And that is due, of course, to the presence of that extra lone pair here, up above one oxygen and here, up above the other oxygen.

And what we have now is a hydrogen serving in a bridging fashion. And the number of electrons in this system is exactly 2 times 8, because we have two water molecules and we have an H plus. So this is a positively charged ion in which a hydronium ion, and you can pick either side, actually, is interacting with one of the lone pairs of the other water molecule. And you could imagine lots of different types of water clusters like this that are singly positively charged. And people have done a lot of work to study such clusters in solution. What you should remember, though, is that the size of the spheres that I have drawn there to represent those oxygens and hydrogens is somewhat arbitrary. But what is not arbitrary is the way that the electron density represents a molecule like this. So, we will show that to you next.

Here it is. And if we could have the lights down just a little bit, please, since this one is a little harder to see. What you should see here is that we have the same structure now surrounding that representation of the water molecule hydrogen bonded to the hydronium ion that I drew a moment ago. We now have this sort of mesh, which is exactly what we have been looking at with these other molecules, namely, an electron density isosurface. And what you can see is that the electron density is falling to a pretty small value in the middle, here, where we have the proton that is the connecting glue binding together these two water molecules in this 16 valence electron system.

And after one more representation of that, we will be onto our next topic. And this one is a solid display of the electron density isosurface associated with this hydrogen bonded cluster. And it is, once again, color mapped with this function that tells us about the probability of finding electrons paired up together in space. There is H three O plus hydrogen bonded to H two O. The blue color represents those regions in space where you are most likely to find pairs of electrons. And you can see that the two OH bonds over here are nicely colored blue.

The lone pair of electrons up here is nicely colored blue. And then we have an interesting situation where there is some blue in between that bridging H plus and the two lone pairs that are pointed at it that produces, in fact, our hydrogen bond. So, there is a picture of hydrogen bonding in terms of electron density. And it is a type of bonding that compliments the straight, covalent, and ionic bonding

that I was talking about in terms of SO_3 and AlCl_3 . So, we have added this third type of hydrogen bonding to our list of bonding interests. And now, we will talk more about what we can do when we consider Bronsted acids ionizing.

Here is a generic representation of the formula of a Bronsted acid, HA. A might be, for example, the HSO_4^- ion that we showed over there. When we put a Bronsted acid in aqueous solution, as I said before, we can get ionization into H plus and A minus. But we know that it is not just H plus. It is actually H_3O^+ . And H_3O^+ is further hydrogen bonded in networks in the water system. But, for simplicity, I will just write it as H plus right here.

Recently, in your crash review of thermodynamics, you were talking about equilibria and equilibrium constants. And we are going to make use of some of that right here because we are going to talk about the acidity constant, K_a . And that is going to be defined as equal to the hydrogen or hydronium ion concentration times the concentration of the conjugate base, A minus -- When a Bronsted acid ionizes it produces what we call the conjugate base of the acid. Here is conjugate base --

-- divided by the concentration of the acid. And this is at equilibrium. And let me just emphasize something so that you don't forget. This is an important piece of nomenclature. These square brackets here refer to concentration, usually in molarity. Okay? So that is what we are talking about. And concentration is something that can be measured. You may be familiar, for example, with the pH meter invented by Arnold O. Beckman and its utility in measuring the concentration of hydrogen ions in solution.

Well, we can make use of information like that to talk about the properties of our Bronsted acids. How can we do that? Well, let's say we are going to take a particular acid such as this one, which is acetic acid. You know the smell of acetic acid if you have ever been in an establishment where they were making barbecued chicken wings. That is the smell of acetic acid. A beautiful smell.

Anyway, what you do here is you are trying to figure out what is going on. You have some concentration of the acid HA, which is, we are going to talk about, acetic acid. And in solution there may also be a hydrogen ion or a hydronium ion. And then there may also be A minus, which in the case of acetic acid would be acetate, -- -- where we have two electronegative oxygens, among which the negative

charge can be shared and the acetate ion, which is the conjugate base of acetic acid. So we make a table. We need to have some initial concentration. That is to say let's consider, for example, tenth molar acetic acid. We are just choosing tenth molar as a concentration for acetic acid solution.

What that means is you have pure acetic acid. And then you dissolve it in water and bring it up to a total volume such that the concentration was 0.1 molar, assuming that none of it had been ionized yet. And so that means we have an initial concentration of acetic acid of 0.1 molar. And initially, before the ionization, we have zero H plus or hydronium and zero A minus. And then, the concentration changes. And it changes because the HA ionizes to some particular extent, depending on the K_A value for the acetic acid. And what is going to happen is that some of the HA ionizes.

And the amount of the HA that is undergoing ionization is x , so we are going to lose x . And then, for every HA that ionizes, we get that same amount of H plus produced and that same amount of A minus. And so then, after the system reaches equilibrium, we will finally have $0.1 - x$ as our concentration of HA and x and x will be our concentrations, respectively, of H plus and A minus.

And so let me put this board all the way up. Therefore, we can write the following, that K_a is equal to x^2 over $0.1 - x$ by substituting into the expression for the acidity constant. K_a is our acidity constant. And we can go to a table and look up the acidity constant for acetic acid because it is a known quantity. And it turns out that that is 1.8×10^{-5} .

And now that we have this equation for the acidity constant and we know what the acidity constant is, we can solve this for x . Of course, this is a cubic equation. We are going to get two roots. You will see that you get a positive root and a negative root. The negative root is meaningless because concentration cannot be negative, so you pick the positive root. And when you have done that, you can then go ahead and answer questions, like, what is the pH of the solution? And what is the percent ionization?

And we can talk about that. So next time, at the beginning of class, we will do that calculation. We will find what the pH of a tenth molar solution of acetic acid would be. We will also go on and talk about pH and the pKa scale, and also a general equation for discussing titrations and buffers.