

## Lab 5A • 10/10/11

### Quiz, first problem

First, if you're formally going all the way to a line structure, in this particular example, you would have gotten rid of all of the carbon labels. Particularly for the triple bond, some of you were nervous about getting rid of the carbon labels for the triple bond because you weren't sure that you were going to be able to show that you had a single bond that then stopped then turned into a triple bond, how do you show there's an atom there. We do it the same way that I had drawn in the examples in class, where you just draw that single bond, and then you can switch to a triple bond. Someone reading the structure would automatically know: oh, there is a carbon there as you switch from the single to the triple. You didn't need to include any of your carbons. One thing you can't do is you cannot leave out the hydrogens on nitrogen and oxygen, because this line structure system is a system for writing carbon. Any presumptions that we make about hydrogens being there or not we only do that with carbon, so you had to write the ones on the oxygen and nitrogen in. Let me draw the answer. There's our carbon framework. We've got 7 carbons. You can see the way I made sure to show the triple bond. A few of you left the carbon where the oxygen attaches out. Some of you tried to attach that to the same position as the triple bond. When attaching that oxygen, you do show a bond. You cannot just write oxygen at the top of the peak; you have to write a bond to it. The only place you could have simplified is to right the O and H right next to each other. Because that's a functional group, because it's so common, if you didn't put a bond in there, it was ok. For the other side, we would need to have the nitrogen. It is the nitrogen that is attached to that carbon. if you write NH<sub>2</sub>, N first, H second, I understood what you meant, but normally, we would write it this way, H<sub>2</sub>N, to make sure the bond is ending at the atom that really is making that connection. If we had the nitrogen here, then we could write NH<sub>2</sub>.

Starting out with a line structure, if we want to write this out, we should write all of the hydrogens, if we're really making a full structure. Some of you wrote the carbons in but didn't put the hydrogens in. Let's figure out how many carbons there are – 5 carbons. Then the heteroatoms, since you never leave those out, whatever you see, you just write. Some of you tried to do something strange with the carbon-oxygen double bond, tried to put another carbon in. On the other side of the double bond, if you have an oxygen, then that is the atom that's located there. You don't insert a carbon there and make a new bond to the oxygen. Translating from the line structure here, the only thing that changes is there is the carbon that you write in, and, because that carbon currently only has three bonds showing to it, we need to put a hydrogen in as well. Look at the other positions on the molecule, the middle carbon already has a double bond and two single bonds to it, so we don't need hydrogens on it, so it's fine. The next carbon over, the first carbon of that triple bond, already four connections to it, don't need a hydrogen. Only the end carbon will need a hydrogen, as well as the carbon up top, which also only had three connections before I threw that hydrogen in.

### Question 2

You were asked to draw an s and p orbital of any energy level and shade your drawing appropriately and explain what the shading represents. I left this wording intentionally vague so I could see whether you would choose the right shading system or not. For atomic orbitals, since we're normally going to be writing them to show how bonding occurs, normally you write them to show the sign of the wavefunction. If you're doing that, an s orbital would be whatever color you happen to choose, then a p orbital would have two different halves, one colored differently than the other. If you said that one half is plus and one half is minus, that's not a complete answer: plus what, minus what? I might think that you're thinking of charge. If you had said plus or minus phase, of what? Plus phase of what, minus phase of what? The complete answer is that the plus and minus are the sign of the wavefunction, so one of those is when the wavefunction itself is negative and when the wavefunction itself is positive. We also have SMOGs in which the orbitals had shading not according to phase, but we weren't using those SMOG diagrams in bonding like we were with atomic orbitals. The only shading I had shown you for atomic orbitals was shading according to sign of the wavefunction.

What's the difference between a sigma bond and a pi bond? If you said a sigma bond is for s orbitals and a pi bond is for p orbitals, that's wrong, because p orbitals can be oriented so that they're pointed at each other. P orbitals can make sigma bonds. If you just said sigma bonds are for s orbitals and pi bonds for p orbitals, that's not a complete description. A complete description would be that the sigma bond is when you have head-to-head overlap, when you have it such that the bond, when you rotate it, remains exactly the same. That could be between s orbitals, or, as we saw in SMOGs, it could be between an s orbital and an sp<sup>3</sup> orbital or an sp<sup>2</sup> orbital or an sp. We also saw that p orbitals, if they're in line, form sigma bonds. What's the difference then between a sigma bond and a pi bond? Pi bonds would be parallel overlap, sideways overlap, which so far we've only see p orbitals doing. You can't just say p orbitals, because they overlap in two different geometries. The real answer focused on the geometry of the bonds, whether it's head-to-head or whether you have sideways overlap.

### Question 3

A functional group is not a molecule. If you say a functional group is a bunch of molecules on an molecule, there's no such thing. There's a group of atoms that are part of a molecule. That group has reproducible or predictable behavior, no matter what molecule it appears on.

### Question 4

You were told that a bond is lower in energy, and you were told that the antibond is higher in energy. You were asked: why is this true? If you said a bond is lower in energy because it releases energy, you just told me that a bond is lower in energy, but you didn't tell me why. If you said that an antibond destabilizes the molecule and that's why it's higher in energy, well why is it destabilizing? There's no concrete answer in that answer. If you tell me that anything to do with the atoms getting closer or further away from each other, you were describing the classical model of bonding. The whole point of going over the classical model was to show that it's wrong, that it doesn't describe what is going on. Here's the real reason. A bond is lower in energy because electrons are placed between nuclei. The more that you get plus and minus charge to interact, the lower the energy of the system. If you have an antibond, you have a node that is between the two atoms. The node means there's no electrons there, so the nuclei are experiencing the repulsion of each other. That is high energy, and that's why an antibond is higher in energy. Some of you had the right answer and then went a little too far: you said it was to do with electrons being between nuclei or not being between two nuclei. Remember that our way of modeling the bond and the antibond, where we add and subtract orbitals, that doesn't happen in real life. Realize that it's not when two orbitals approach that they add and subtract, that's what we do on paper to make things that look that like the bonds and the antibond. What happens physically is just the wave's pattern changes because of the influence of the two nuclei. These models are all fake. A bond is lower in energy because the bonding orbital places electrons between nuclei, increasing interaction of plus and minus charge. The antibond is higher in energy because the molecular orbital has a node, where there are not electrons between nuclei, which means the nuclei are exposed. Yes, it's true the nuclei are going to repel, but that doesn't have anything to do with distance, per se. It's not that the atoms get too close and now there's an antibond. When you form a bond, that fixes the distance between nuclei. Then, if you have an antibond, it's for that same distance. That distance will disappear if you have an antibond filled, because then you'll break the [bond] apart, which is the next part of the question: why does hydrogen exist as a molecule but He<sub>2</sub> does not?

If all you did was to write this diagram, even if you labeled it, how do I know from that you know what the answer is? You know the diagram, but what's the meaning of it? You have to tell me that, in hydrogen, only a bonding orbital is filled, and that lowers the energy of the system. That's why a bond forms. For helium, the bonding and antibonding orbitals are filled, so the antibond cancels out whatever stabilization the bond had and that's why the molecule won't form.

### Question 5

Why do atomic orbitals fail to describe a molecule? The why is not because they're not all the same energy and because the geometry's wrong, that's how they fail. Why they fail is that atomic orbitals only exist with exactly one nucleus. If you have multiple nuclei, you don't have atomic orbitals, that's why they fail. The examples you were asked for were related to methane. P orbitals do have the wrong geometry; methane is 109.5°, p orbitals are 90° angles. Atomic orbitals are different in energy; the bond orbitals in methane are all equal. Those are the two ways in which you see how atomic orbitals fail. How do you make hybrids? The how is not count up the number of sigma bonds and lone pairs; that's how you know how many hybrids there are. The hybrids themselves are created by adding and subtracting atomic orbitals.

{reminder of Parts A and B procedure and directions for analysis and waste disposal}

### Melting point theory

Most solids have what kind of internal structure? If I had one word I wanted to describe solids as. Crystalline. What does crystalline mean? Uniform geometric arrangement. When we think of the word crystal, we think of some kind of bling on a ring, but that just means that you have a large amount of that solid that's very highly ordered throughout the solid. Crystalline, in terms of solids, does not mean sparkly kind of crystal; it means, geometrically, the molecules [or atoms] are in a regular pattern. {description of nobel prize relate to semicrystals awarded in 2011} Crystallographers used to think for something to qualify as a [true] crystal, that shape had to exactly repeat somewhere along in the structure. If you took a copy of the arrangement of molecules and moved it over on paper, the theory was, you had to be able to find that repetition somewhere; that's called translational periodicity, repetitiveness. These quasi-crystals don't have that but they were thought to have some form of symmetry, it was thought that they can't exist, until someone went along and proved they did. That's related to this idea that solids have some kind of geometry structure to them. if you don't have that, what kind of solid is that? Amorphous. A few solids do form that kind of pattern. Sulfur, for example, can have an amorphous form, where there is really just a total random arrangement of atoms. It's the exception, not the rule, though; most solids are crystalline.

What happens when something melts? Highly idealized, we might have a drawing for a solid like this, where if we imagine the molecules are rod-shaped, they'll try to pack together as closely as possible. In a crystalline solid, you'll have some kind of ordering of the molecules. What happens when a solid melts? What's going on? Molecules are spreading apart, bonds are breaking? Are bonds breaking? No! Bonds breaking is a chemical change; melting is a physical change; it doesn't necessarily have anything to do with a chemical reaction. What you meant is that the associations between molecules are breaking down, these intermolecular forces that we've talked about, something is overcoming them. But there's a difference between a force and a bond. The intermolecular forces are just attractions. If we had bonds between molecules, you'd just have one big, huge molecule. That's what bond means. Melting does not involve any bond breaking. Melting occurs when thermal energy – the fact that, at room temperature or any temperature, molecules are wiggling around – melting is when that thermal energy overcomes the ability of the intermolecular forces to keep molecules stuck together. When thermal energy, which means internal kinetic energy, exceeds the ability of the intermolecular forces to hold molecules together, a phase change occurs.

The box is representing a crystalline solid.

{description of using a mel temp}

You have a base that contains the heating element. That heat is transferred up through the apparatus. There's an observation window, so when you stick your samples in, you're going to be watching to see if it melts or not, and you've got the thermometer that gets stuck in the top of the device.

Thermal equilibrium

If you have a hot object and a cold object, what goes on when they contact? The hot object has molecules that are moving quickly; the cold object's got molecules that are moving slowly. What happens is that the hot molecules, the faster-moving molecules, bump into the slow ones and just from the fact that they collide into each other, at some point they all wiggle with the same amount of [average] energy. But that is a physical process, therefore it takes time. Thermal equilibrium is a state in which the molecules all have the same average energy, but it takes to achieve that.

If I was impatient and wanted to get this melting point over with in a hurry, I might be tempted to turn the heat all the way up on the MelTemp device. If I did that, what's going to happen to the temperature reading I might get? In this specific case, given this apparatus, will the melting point change? The answer is no, your observation of the melting point will change. Melting point doesn't change just because your heat source changes; what you see changes. When we observe a change in the melting point, will it go up or will it go down? You got two choices, which one is it? It goes down, why? The heat will not have made it up to the thermometer in time but your sample will have already melted. That means that the thermometer will be at a lower temperature than what your sample will be when your sample melts. Because heat takes time to travel, because of thermal equilibrium, if your thermometer is further away from the heat source, then as this heat is radiating on up, the same melts, but the thermometer hasn't been heated up enough yet. I want to emphasize it has nothing to do with how much heat is being put in; that does not change the melting point. But because this is a physical system in which it takes time for heat to travel, that's why things appear to change. In this particular experiment, if a solid is heated too rapidly when measuring melting point, the melting point will appear to lower, since not enough time was given for the thermometer to reach thermal equilibrium, which is a condition in which all molecules have the same average energy.

Ideally we would heat a system up for melting point one degree per minute. There are machines that are automated that can do that for us. For this equipment, there is a problem. If we're at room temperature (~25°C), and if you needed to measure a solid with a melting point of 120 °C, that means it's going to take 100 minutes to complete that melting point. What can we do? Why wait an hour as we wait for the temperature to crawl from 80 °C to 81 °C to 82 °C, when nothing's going to happen until you're well above 100 °C. So, crank it up at first, turn the heat up high, but as you're getting close to 100 °C, slow way down. Depending on how high you turn it, if you take me too literally, and you turn it up to the maximum setting, realize that that thermal equilibrium means there's a time lag. Even if you pull the plug and turn the power off, there's still heat radiating, so the temperature will continue to rise even once you turn it off. Do it carefully enough, you can get up 100 °C and then slowly heat. If you got up to 105 °C and then heated at two degrees a minute, it's only going to take you 10 minutes to do a melting point.

If we didn't know the identity of the solid? We do the same thing: crank it up. We then realize that, when you see it melt, it's going to be too low, so you then you do it again. Say it melted at 160 °C, the slow down at 150 °C or 140 °C, because you know whatever the real temperature is, it has to be higher. Since we know [for this compound] that it's 122 °C or slightly below, heat rapidly up to about 100 °C; by the time things stabilize, you'll be at 105 °C, 110 °C. Then, if you go really slowly, you get a nice, accurate melting point.

Why do we care about getting a nice, accurate melting point. Because it [can tell] us something about the purity of the sample that we just made. It is a rudimentary technique. We would never use melting point itself to prove anything, because we have much more sophisticated ways of verifying a compound's identity.

Back in the old days, 100, 200 years ago, melting point was one of the ways that we did things. Historically, that's why we're still carrying melting points around, because there are so many compounds that have had their physical properties tabulated.

If you get a melting point of 122.4 °C, that means you've got benzoic acid. If you get a melting point of 120 °C, there's two choices of what that means: you did it too fast, you were in too much of a hurry; or, you had an impurity. Why does having an impurity cause the melting point to drop? If you put an impurity in there, you're going to interrupt this internal structure of the crystal. What does that do to the intermolecular forces between the different molecules in that crystal? It weakens them. If it weakens the intermolecular forces, and melting is the point where you get over those intermolecular forces, if you lower your target, you don't have to put as much energy in. By disturbing the crystal structure of a solid, it makes the attractions between molecules easier to overcome, which means less energy has to be put in, so the melting point is lower. This melting point depression.

Picture-wise, it would look something like this. Parts of your solid are really well-packed, still, but every once in a while, you've got this impurity that's stuck in it. Technically, we're talking about solutions, we're talking about colligative properties, we should be very careful to say that the solute and solvent are the solute and solvent, that there's solubility going on. In this case of recrystallization, what can happen is that water, even if it's not soluble, might get trapped as part of the crystal structure; we call that a hydrate. You might have some water going along for the ride with your benzoic acid. That's why, hopefully, you finished your recrystallization last time so that you had this whole past weekend with it sitting around air drying, so hopefully you don't have that water. Because that impurity interferes with the intermolecular forces and decreases them, not as much energy is needed to overcome them, which means melting occurs at a lower temperature.

That brings up some important points: how do we know if something has melted? What are we observing? You'll have a sample that you'll load into a microcapillary – basically, a really tiny, itty bitty test tube. You'll take the single open-ended capillaries, which means the other end is closed, so that when the stuff starts to melt, it doesn't just dribble into the machine. You take the open of that capillary tube and carefully tap it into the solid sample, which means you're going to get the top portion filled up with the solid. You can then use a hollow glass tube, where you'll put the tube on your benchtop and drop the closed end of the sample down and bounce. It just happens to be that that shock of bouncing from that height is about the amount of force you need to get that solid to go down into the bottom of your capillary. Some solids might not work as well; you might have to manually do it; it just might be a little more resistant. That's the easiest way to load the samples.

That little capillary, there'll be an observation window and a place to put your sample in there, and then you're going to watch your sample as you increase temperature. In connection with a compound possibly incorporating some water: around 90° or 100°, you might see your sample sweat, which means that liquid will appear to start to form, but it won't be the whole sample that starts to melt; it's just water possibly coming out. You might see it crinkle a little bit, you might see a change in its translucency just slightly, but then continue to stay the same – it's that sweating phenomenon, it's just water coming off. When it really melts, you'll see the whole darn crystal start to crumble and to liquefy, to move, to become more transparent. Even if you're doing it carefully, you might see just one temperature at which it melts. That's because, in a real crystal, because you might have molecules slightly differently arranged, some might melt before the other, but over a very narrow range. So, from the temperature the sample starts to melt to when you see the last bit convert to liquid, that's the melting point range, and yes, you should mark both the beginning and ending temperatures down.

Once you've melted a sample, if you need to make another melting point, you have to make a fresh sample. Although it likely won't happen for benzoic acid, it is possible for some solids to melt, freeze, and then melt at a different temperature than it did the first time. That can happen if, once it melts, the molecules rearrange, compared to what they were in the solid originally. Generally, that only happens with polymers, systems with very large molecules. But, since I'm teaching you a general technique, in general, you've gotta toss your sample after you melt it. These little capillaries can go into the waste bottle; it is fine for solids to be put in a bottle labelled liquid, but not the other way around.

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#### Solids

- crystalline – has a periodic, ordered geometric pattern
- amorphous – “without shape” – no regular crystal structure

When thermal energy (internal KE) exceeds the ability of the IMF to hold molecules together, a phase change occurs.

In this experiment, if a solid is heated too rapidly when measuring the melting point, the MP will appear too low, since not enough time was given for the thermometer to reach thermal equilibrium, which is a state in which all molecules have roughly the same energy.

An impurity will interfere with the IMF between molecules in a crystal, causing lower IMF. Less energy is therefore needed to overcome the IMF, so the MP is lower.

Structures

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