

## Lab 5B • 10/11/11

This is problem 1 from the quiz. Let's tackle the bigger problems first. As far as writing in carbon labels, if you're really making a pure line structure, you wouldn't leave any of the carbon labels. If you did write the carbons in on the triple bond, it's not really an incorrect structure, particularly if you were trying to highlight some reactivity of one of those carbons that's part of that triple bond. But, if you were fully converting, you would leave all of the carbon labels out. So, if I wanted to write the carbon backbone structure, it would look like this. The reason some of you might have put labels in for the triple bond might have been that you were worried about whether or not I knew what you meant by writing a single bond and then suddenly switching to a triple bond. But, this is the way it is done. If you're worried about making it clear enough, sometimes you'll see structures with a little dot written at the junction between the single and the triple bond, to show there really is an atom there. For the future, unless you are showing something about a particular position, just leave all of the carbons out. You can't leave out the hydrogens on the oxygen or nitrogen, because the writing system is for simplifying carbon, but it doesn't make any presumption about what's on any of the heteroatoms. Those hydrogens you had to write in, although if you wrote them in condensed form, that was fine – condensed meaning not showing the bond between oxygen and hydrogen. In fact, that's what I'll normally do in focusing on them as functional groups.

For the nitrogen group, it is really more correct to write H<sub>2</sub>N, because the carbon is attached to nitrogen, not to the hydrogens. If you wrote NH<sub>2</sub>, it might be viewed as you trying to say the connection is between hydrogen and the carbon. Most people would know what you meant, but to look more sophisticated, you'd write the nitrogen towards where the bond is connect. Notice there is a line between the carbon and the oxygen in this alcohol. Here, if you just wrote –OH with no connector line – you do still show the bonds between heteroatoms and carbons. A few of you accidentally interpreted the end of this triple bond as having a methyl group on it. For hydrogens, you leave the bonds and the atom labels out, so there wouldn't be anything you'd need to include here for that triple bond; just leave it blank on the end.

Going the other direction. If we're counting carbons, everywhere there's a zig-zag or you change the direction of the structure without anything written, that is a carbon, so it's got 5 carbons on that molecule. I'll again leave the nitrogen written in condensed form. Notice that the carbon oxygen bond remains just a carbon-oxygen bond. A few of you thought that over here, where the oxygen was located, that there should have been another carbon, but in the line structure, you wouldn't show another atom, unless that is what the bond was being connected to. If the oxygen really was connected to yet another carbon, there would need to be a line between the carbon and oxygen showing that bond. So the carbon-oxygen bond stays the same. On the carbon, you would need a hydrogen, because as it currently stands, there's a double bond and a single bond, which means only three connections, so you'd need one more hydrogen. There are only two other places that need hydrogens, because the middle carbon already has two singles and a double bond, so that's four connections. Over here a single and triple bond; that's four connections. And then, at the end, because we only have the triple bond so far, you do need a hydrogen, and on that top carbon, since there's only three connections so far, you do need a hydrogen.

Problem 2. First, you were asked to draw an s and a p orbital and then you were asked to shade the drawing appropriately and explain what the shading meant. When we drew atomic orbitals, we drew them to show the phase of the wavefunction. Many of you said it represents where it's plus or minus, but plus or minus what? I could think that you're thinking charge. You had to say plus or minus sign of the wavefunction; that's what shading of these mean. Some of you misinterpreted this as a SMOG diagram; those really were two different discussions we had. We had atomic orbitals, where we hadn't even seen the shading for SMOGs yet, and then we had the SMOG diagrams themselves. Whenever we're referring to just the atomic orbitals, this should be the way that we shade it. S orbitals, any color that you want; the p orbital, the two halves have to be different because those are the two different signs of that wavefunction.

You're asked to explain the difference between a sigma and a pi bond. If you said a sigma bond is between s orbitals and a pi bond is between p orbitals, that's wrong. We saw that two p orbitals can line up with each other head-to-head, and that would form a sigma bond. If you just say a pi bond's pi orbitals, no, because you've got to say how are those p orbitals oriented. If you say a sigma bond is just between s orbitals, you're ignoring the case of the p orbitals overlapping, or, bringing SMOGs into the discussion, we've seen plenty of single bonds between things that aren't s orbitals. The best way to answer that question is to say a sigma bond is one where you have head-to-head overlap, or that when you rotate the bond, the bond does not change. For pi bonds, it's best to say that that's due to parallel overlap, side-to-side overlap, or to say that there's a node through the bond, so as it rotates it changes.

Moving on to problem 3. A functional group is a groups of atoms that has predictable behavior, reproducible behavior, no matter what the molecule it's attached to. Some of you said that they're molecules attached to molecules, which, if you did have that situation, it's really just one big molecule. You need to say that it's some subset within a molecule, this group of atoms that has the predictable behavior.

Problem 4. Here's the answer you could not give me: if you said that a bond is lower in energy because it's more stable and an antibond is higher in energy because it's unstable, what you really just said is that a bond is lower because it's lower, and an antibond is higher because it's higher. It's not a complete explanation; it doesn't tell me why it's lower and why it's higher. Why stabilization occurs for a bond, why does destabilization occur for an antibond. If you said almost anything about how far or close the atoms were to each other, you were talking about the classical view of bonding. The whole point of presenting that was to then say that's not the complete view. We have to look at it as waves. The correct answer was this: for a bond, you've got electrons between the nuclei. Since that increases the amount of interaction between plus and minus charge, that's what causes the lowering. For an antibond, it's because you don't have electrons, you have a node between the nuclei, which means the nuclei are exposed to each other. Whenever like charges interact, that's unfavorable, that's increased energy. That's why an antibond is higher in energy. If you have two plus charges here, what's in between? If you have electrons between, then that's going to keep the two nuclei together. If you had the individual atoms, where the electrons purely were just around each atom, then you could say nothing's going to happen, because they're already charge-satisfied. As they approach in the quantum model, we imagine that there is this bond thing that forms. Since the electrons are localized between the nuclei, that's more attraction between plus and minus charge than they would have had if they were separate, and that's why it's lower. For the antibond, because you lack the electrons between, not just lack them, but if you look at the shapes of the orbitals, the electrons are actually pushed outside of the antibond, so the nuclei are in the middle and the electrons are on the outside. If anything, the atoms would want to be pulled apart. Since the bonding orbital always fills up first, you're going to have the nuclei at some set distance. Then, if you try to fill the antibond, because they're at that distance and there's no electrons bridging the positive charges, there's then going to be that unfavorable interaction of charge, which causes it to be higher in energy. It's not because they're closer or further; I avoid that terminology because that sounds like a classical description. A bond forms and the nuclei are a certain distance from each other. At that same distance, if the antibond tries to form, they're close enough that they'll interact, which means that they want to repel; that's partly why an antibond causes a molecule to fall apart.

The other half of the question was why does hydrogen exist and helium does not? It has nothing to do with one's a particle, one's a wave. The entire problem is about waves, not whether it's a particle versus a wave. For hydrogen, the reason it does form is cause the bonding orbital fills up first. So, there's a bond in hydrogen, but no antibond, so it can exist as a molecule. For helium, it doesn't have to do with the octet rule (or the duet rule). That is an indirect way of explaining it. The real reason is that if you make them interact, you make a bond and an antibond. The antibond cancels out whatever stability the bond would have given you, and so no molecule results. If all you showed me was this, that is exactly the right drawing to use, but if you said nothing, I don't know if you knew that's what it meant or not. I said a couple of points in the quiz that drawings alone are not adequate. You need to at least show that bond order calculation or at least show to me that this is representing a bond and an antibond. You can show the pictures of the real molecular orbitals. A bond would be like this, just a blob with a node in it, and an antibond would look like this. If you're trying to answer the question using p orbitals, what you'd say is that between the atoms there's still electrons in the pi bond; yes, there's a node, but the atoms go through the atoms themselves. In the antibond, though, there's just no electrons between the atoms at all, so repulsion of nuclei, which means higher energy.

Question 5. You were asked why is it that atomic orbitals fail to describe a molecule. You were then asked for ways in which you could show how it fails. Those are two different questions, then: one is why does it fail, and the other part of that is in what ways does it fail. Atomic orbitals fail to describe molecules because there's multiple nuclei. Atomic orbitals only exist if you have just one nucleus. That's the why. How does that manifest? In methane, we saw that there's supposed to be  $109.5^\circ$  angles, but we only end up with  $90^\circ$  for the atomic orbitals, so that's a mismatch. Then, in terms of energy, all of the energies need to be the same in those different bonds, but the orbitals themselves are different in energy. Those are the two ways that atomic orbitals fails; it's because of the number of nuclei around. How are hybrids created? By adding and subtracting atomic orbitals. To emphasize, it's not because atomic orbitals treat things as particles, because if you say the word orbital, it automatically is saying wave. There's not such thing as an orbital for a particle.

{description of lab procedure and waste disposal}

Sometimes all it takes is a trace of a compound to really color a solution.

You can add water to the layer, and if it just gets incorporated into the layer, you know that it's aqueous, and if it makes a layer, you know you just added it into the organic instead.

#### Melting point theory

You might ask why we are doing melting point when we have all of this fancy instrumentation these days that would much more concretely identify the structure of a compound. Roll back 100 or so years ago, melting point was one of the only ways that we could identify a compound. That's why there's so many compounds that are tabulated for their melting points. Because it is a relevant piece of physical data, we do still measure the melting point whenever we're reporting a new compound. It is sort of an after-thought, final check of the compound. We can use melting point to assess the purity of a compound.

To start with, we need to talk about the structure of solids. Most solids can be classified as what type of structure? What's the arrangement of atoms or molecules in most solids? A lattice or a crystalline pattern. A crystal doesn't necessarily mean something shiny that you put on your ring; crystal means a regular, repeating pattern of atoms. One of the [recent] Nobel prizes had to do with crystallographic analysis, which has to do with crystal structures. Most solids are crystalline, which means they have a regular or periodic geometric arrangement to the atoms or molecules in the solid. That doesn't mean that the entire solid has to be perfectly aligned. Instead, we normally have domains, regions in which there is that alignment, but then right next door, there might be a little area that's just at a slightly different angle, then you have another area, then another area. That's why most solids don't look like these nice, shiny crystals; they have such a variety of domains. What's the opposite term? What would you call a solid that doesn't have this arrangement? Amorphous, which literally means without shape or form; it refers to a solid without any internal structure.

Since the vast majority of solids are crystalline, we'll limit this discussion to that. I'll use this very idealized picture to talk about the structure of a solid. You can see that we've got a set of molecules that I've represented as just rods that are trying to pack as closely to each other as possible in the solid. What would cause the solid to become a liquid or a gas? [trr] What kind of energy would be involved in getting a substance to melt? Thermal energy, which is what? It's this wiggling of molecules. What is that wiggling overcoming? IMF, intermolecular forces. So, the intermolecular forces, which are due to polarity, due to plus or minus charges, those bring the molecules together. Then, you have thermal energy, which causes them to wiggle, and if they wiggle enough, if there's enough thermal energy, then it overcomes the intermolecular forces and some kind of phase change can occur.

There is a time factor. There is such a thing as thermal equilibrium, which is the point at which all of the molecules in the sample have roughly the same average energy. I say average energy, because at any temperature, you're going to have a distribution of energies. That's the reason we have vapor pressure, because even at room temperature, some molecules are always moving fast enough that they can turn into vapor. This thermal equilibrium occurs when hot and cold objects come together just by the contact of the molecules in those objects. A hot object – that means you're going to have something where the molecules are moving quickly; a cold object – that means you're going to have something where the molecules are moving much more slowly. Well those two bump into each other, energy gets transferred, and then they both end up moving with about the same pace. That means you need time for that energy to be transferred, since it is a physical interaction. I bring this up because of the device we're using to measure melting point.

It's really nothing more than a box that has a heating element, and an assembly that holds an observation window – so you can see the sample melt – and a place to put your thermometer and your samples at the top. This assembly's got a lot of open space to it. That means if you turn the heat up way high down here at the heat source, get it hot really quickly, it may take a while before that heat gets fully transmitted up to where the thermometer is. In other words, it takes time for that thermal equilibrium to be established. Heating really should be done at no more than one degree per minute. [Benzoic acid MP 122 °C] If we started off at room temperature and then heated it up the way I just described it, it would take us 100 minutes to do one melting point [of benzoic acid]. What can we do instead [to speed it up]? We cheat. In this case, we know what our compound is. We don't need to heat slowly up to 120 °C; what if we crank the temperature up, let it heat up real fast, but then once it hits 100 °C, slow that pace way down. When you do that, you'll still have an increase in temperature occurs, because the moment you cut the power, there's still that heat that's trying to radiate up and establish an equilibrium. You shut the power off at 100 °C, it may still climb to about 110 °C, which should still be comfortably below where you see the melting point. At that point, you could then turn the power on at a much lower setting and more easily, more carefully come up through that melting point and maybe only spend 10 or 15 minutes for the entire process.

If you didn't know the identity of the compound, you could do something similar, where, not knowing where it's going to melt, you crank it up to a relatively high temperature and then see where it melts at. Do you think that that first measurement would be higher or lower than what the real melting point would be? It's going to be lower, why? If you turn the heat way up at the bottom, will the melting point change? No, because the melting point's just a physical property of that compound. It doesn't matter how fast you're adding the energy in, it's still the same temperature that it melts at. Back to the previous question: why would the observed melting point be lower? Maybe it's impure – that's a separate issue, but that otherwise a possibility. The samples are in a lower position than the thermometer is. You turn the heat up on high blast down here, heat starts to radiate, it gets to the compound, the compound melts, but the heat hasn't fully made it up to the thermometer yet, so it's that issue of thermal equilibrium. When taking melting points, heating has to be conducted at a slow pace to make sure the entire apparatus is at thermal equilibrium, otherwise, for this specific device, the compound can get to the melting temperature before the thermometer actually measures it. Too rapid heating is going to guarantee you a too low melting point.

Even if you do everything correctly, depending on how large your sample is, it's always possible you might have a melting point range. That's because of these domains. You might have small portions of the solid that have molecules that are ever so slightly differently arranged than others. If you see a range, which means you see it start to melt and you heat it slowly and it doesn't all melt at once, then note when does it start melting, when does it stop melting. How do you know something is melting? You're going to observe through that window and, way below the melting point, you should see the crystals.

At about 90° or 100°, there is the possibility that the compound may sweat; there may have been small bits of water, even after all the air drying that you did, stuck around on the compound – think of a hydrate. Once you reach 90° or 100°, you may push the water off, so it may appear to crinkle a little bit, but you still see crystals, you don't see it melting. That's a false melting point, this sweating effect. As you continue to heat, when it really starts to melt, you'll see the solid contract, you'll see it turn into a little puddle of liquid. It'll probably get more transparent or translucent. You might observe it over a range.

One way of assessing purity is to observe a compound's melting point, because if it is impure, it's going to have a lower melting point than it should. Why is that the case? Colligative properties. If you have a certain crystal structure the compound wants to form, when you put an impurity in it, you interfere with that structure. To make an extreme example, what if you had some giant molecule that was getting in the way of those other target molecules from aligning? You're dropping the extent of intermolecular forces between target molecules. If you drop the intermolecular forces, that means you don't have to add as much energy to overcome them, that means you've got a lower melting point. Generally, this refers to soluble impurities, if we are purely talking about colligative properties. But, if you get some water trapped in in the form of a hydrate, that also can interfere with the molecular structure. Since we're just talking about solids, not solutions, we can get away without referring to that solubility aspect of it. When an impurity is present, it interferes with the intermolecular forces of the target compound. More specifically, it lowers those intermolecular forces; if you've got a molecule in the way, you can't bring the ones you want together, which means they're less tightly held, which means less energy is needed, therefore, to overcome those intermolecular forces, and so the melting point is lower.

{description of microcapillaries}

Gigantic molecules. It has to do with how the molecules wrap around each other in the solid. If they change configuration when they melt, then when they freeze again, they may again melt at different temperature.

---

#### Solids

- crystalline – having a regular or periodic arrangement of atoms or molecules
- amorphous – “without form” – refers to a solid without any internal structure.

A phase change can occur when KE in the form of thermal energy is able to overcome the IMF.

Thermal equilibrium – the point at which all molecules in a sample have roughly the same average energy.

When performing melting points, heating must be conducted slowly (ideally 1° C/min) to ensure the entire device is at thermal equilibrium. In this lab, if heating is conducted too rapidly, heat will reach the sample before the thermometer, so the sample will appear to melt at a lower temperature.

When an impurity is present, it interferes with the IMF of the target compound (lowering the IMF). Less energy is needed to overcome the IMF, so the melting point is lower.

---

#### Structures

Identical to those from lab 5A (10/10/12)