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3.091SC Introduction to Solid State Chemistry, Fall 2010  
Transcript – Exam B Problem 11

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PROFESSOR: OK, welcome back. We're going to be looking at problem number 11 in the fall 2009 final exam. This is one of those problems on the exam that kind of tests a whole bunch of other stuff we couldn't get into one big question. So it's looking at a bunch of different areas. But the main themes are going to be bonding and reaction rates and half lives. So the things I think you need to know, the W I N list as I usually call it, you need to understand reaction rate orders. What they mean, how they apply to reactions. What a half life is and how you use that. And the third thing is melting points and how they are related to intermolecular forces and how intermolecular forces affect melting points. So review these three things and once you've got them under your belt then let's attempt the problem.

So let's start the problem. The first part is asking us to determine the half life for a particular reaction. So there's two places you could start. We saw both answers. You could start with the definition of half life. If you've got it down on your equation sheet, you could just say, well I know this is the equation which is the natural log of the starting concentration--  $c_0$  naught-- divided by the current concentration that you're looking at--  $c$ -- equals  $kt$ , where  $t$  is time and  $k$  is your constant for  $k$ . Or your reaction rate constant.

Or-- and this is the place that I would recommend starting because it's universally useful to use for doing kinetics problems and also for doing half life decays-- you start with your rate equation. This is a very general rate equation, which I'm going to show you how it can be transformed to solve this very simple problem. We're told here that we're looking at the half life of a particular reagent, it's not listed. And we're also told that it falls by factor of 11 in 11 minutes. Because we're looking at one material, we don't need two different items. So we're just going to look at a. Let's forget about b. There's no b. OK, we're just looking at how a changes over time.

We're also told that it's first order. So we're given this information in the problem. First order means that you have an  $n$  equal to 1. So  $n$  equals 1, which turns this equation into  $k$  times the concentration of species a. We also know that rate is nothing more than the changing concentration with respect to the change in time. So in calculus that would be  $da / dt$ .

So looking at this now, we've already got a differential equation, which we can solve and given certain boundary conditions we can apply as a naught as our starting concentration, we can create a new equation. So the way we're going to do this is we're going to do the calculus-- which I'm not going to do for you here-- it's very simply you're going to find this equation. This is all coming from the very general rate equation that we started with. So there we are. That's where we're at and you'll

notice if I bring this  $a$  to the other side, I take the natural log, I put a negative sign in there, I return back to my original equation that I sort of luckily-- or didn't luckily-- have on my equation sheet.

So now we've got this equation. And now we can actually go ahead and solve the first part of the problem very easily. So I'm going to move over here. We're going to start off. We're going to say we're told that in 11 minutes we have now  $1/11$  of the concentration we originally had. So let me write that mathematically for you. I'm going to write a naught as my starting concentration of  $a$ . So in 11 minutes we're going to have  $1/11 a$  naught  $a$  naught  $e$  to the negative  $k$ . And that occurs in 11 minutes. Just express the statement mathematically. We've can cancel out these  $a$  naughts so they don't matter. Which is good because we don't know what it is in the first place. And now we can rearrange this equation pretty simply. We can just do it as, solve for  $k$ , our reaction rate constant. That's going to be negative  $1/11$ , natural log of  $1/11$ . That's  $k$ .

And now we have a value for  $k$ . Now that we know the value for  $k$  we can go back and find the half life. And half life is simply defined very, very similar to how we approached the problem to begin with. Half life is how long it takes for the concentration to drop from its original value to half of that original value. So let me write that now in mathematical terms.

In this problem we know  $k$  now but we don't know the half life. We don't know  $t_{1/2}$ . I'm going to call it  $t_{1/2}$  to designate it and to mark it differently than before. Again we can cancel these off. And now we can solve. Because we know  $k$ . So let's plug in everything. We can reverse everything. So let me do that for you. We're going to have this. Natural log of  $1/2$  being equal to negative  $k$ ,  $t$  to the  $1/2$ . And now we can solve for our  $t_{1/2}$  because we know that  $k$ -- let's bring  $k$  to the other side, and the negative sign as well--  $k$  is going to be negative  $1/11$  natural log  $1/11$ .

We can then change natural log  $1/2$  into natural log 2. That actually looks like our original half life equation if you had that on your equation sheet. So when you solve this out, you're solving for  $t_{1/2}$ ,  $t_{1/2}$  the long and the short of it is 3.18 minutes.

The main takeaway from this problem is that you don't need to have memorized any number of equations to do it. You can start from a very general equation, which is the rate equation, which we showed in the beginning, and go from there using logic and then just mathematically represent what the problem is telling you to do in the first place. So that's part A and that's the majority of the points on this problem.

Moving over, part B and C are very quick, very short. Just to check if you know the facts. Let's do them right now. We're asking you-- we're going to do B 1 and B 2 together-- to tell us which one of the compounds has a higher boiling point. And we give you two different cases. In each case there's two compounds.

So number 1, you're given silene and phosphene. So the first thing you should do is actually draw those molecules out. So that's what I did. Silene looks like this. And then phosphene-- put the bonds in there-- phosphene looks something like this. So now we have to sort of identify which one of these has a higher melting point. Now in order to do that you need to have reviewed and know that melting point is related to the intermolecular forces between the between the molecules. The forces between the molecules are dependent on both their geometry and their chemistry. So

knowing that, if something has stronger intermolecular bonds, it'll have a higher melting point.

So let's take a look at these two molecules. Which one has stronger intermolecular bonds? We have in silene case, we have van der Waals forces, they're generally very weak. We've got those too for the phosphene. But in phosphene we additionally have a dipole. We have partial-- we put maybe delta minus here and delta plus here and here on this side. So our molecule is actually polarized. There's a plus region and a minus region. And because of that you have much stronger intermolecular forces between the phosphenes then you do the silenes. And because these have stronger intermolecular forces, this one has a higher melting point.

The last part of the problem, part 2. We try to throw a little trick in there with you. We look at ammonia and phosphene. So now we're doing  $\text{NH}_3$  and  $\text{PH}_3$ . And they actually both look identical in terms of their geometry. So let me do that now. It actually looks tetragonal if you were to draw the structure out. There's ammonia and here's our phosphene again. You can tell they look the same.

So I think you have to sort of reason out which one has the higher melting point, which is the same thing as saying which one has stronger intermolecular forces. A very common answer we got was that the nitrogen is a smaller atom, therefore everything is held more closely, therefore the forces are stronger. That's not really the answer that is most dominant and it's also not the answer we were looking for. The correct answer here is that even though both of these have the same-- probably very similar-- van der Waals forces, they're both polarized molecules, nitrogen has hydrogen bonding. So remember the hydrogen bonding elements you should probably know are fluorine, oxygen, chlorine, nitrogen, four of them. So nitrogen will hydrogen bond, which means that this nitrogen will have a hydrogen bond with some other ammonia molecule over here. This H might be bonded to an N somewhere else. And because there are additional hydrogen bonding force in the system, the intermolecular forces are stronger and more prevalent in ammonia, which means that ammonia will have a higher boiling point, which is true. The answer here is ammonia.

So all you have to take away from this is that the mechanical properties as well as the melting and boiling properties of a material are very much governed by the intermolecular forces that exist in that particular material, that the liquid or the solid state. And so in this case we're looking at these compounds and we've identified this one as being a higher melting point because it has a polarity whereas this one doesn't. And in this case where we try to trick you up, we identified that nitrogen has this additional hydrogen bonding force. And that's all there is to it.

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