MIT OpenCourseWare
http://ocw.mit.edu

5.112 Principles of Chemical Science, Fall 2005

Please use the following citation format:

> Sylvia Ceyer and Christopher Cummins, *5.112 Principles of Chemical Science, Fall 2005* (Massachusetts Institute of Technology: MIT OpenCourseWare). http://ocw.mit.edu (accessed MM DD, YYYY). License: Creative Commons Attribution-Noncommercial-Share Alike.

Note: Please use the actual date you accessed this material in your citation.

For more information about citing these materials or our Terms of Use, visit: http://ocw.mit.edu/terms

And we saw that we could make a molecule between two inert gas atoms like argon 2 or xenon 2 by virtue of these dispersion interactions where the instantaneous charge in one atom or molecule produced a dipole.

That dipole then induces a dipole in the neighboring molecule, and the result is a stabilization, an attraction. And we saw last time we had a generic form for the interaction potential for the dispersion interactions.

This Lennard-Jones interaction potential. We talked about that in detail. And one of the parameters in that Lennard-Jones potential was this quantity epsilon, which actually was the well depth. And I just wanted to talk a few moments here about what determines what the well depth is, what the strength of that interaction is.

And the bottom line is what determines that is the polarizability of the atoms or the molecules that are interacting. And we give the symbol alpha to the polarizability. And what that is, is a measure of the ease with which a charge distribution can be distorted.

That is the polarizability of the molecule. That is a term you will hear in future courses quite a lot. And, in general, the polarizability goes up with the number of electrons present. As you go from -- And you can see on the side slides here.

As you go from helium to argon to xenon, and let me fix my pointer. As we go from helium to argon to xenon, this polarizability goes up because the number of electrons are going up. If the number of electrons are going up, that means we have electrons in outer shells, they are farther away from the nucleus.

They are more easily distorted. As this polarizability goes up, helium, argon and xenon, that well depth for the Lennard-Jones potential is going up, 0.085, 0.996 and 1.8. And here, on this diagram, I actually show you what the shape of the Lennard-Jones potential is.

Sometimes when I draw it on the board, it is not so accurate. But you can see this Lennard-Jones potentially actually has this repulsive wall that goes up really very steeply. And, likewise, on the next slide you see some interactions for at least one molecule here, helium, nitrogen and argon.

You can also have these dispersion interactions, and you do have them, between molecules. So, the polarizability is going up. Helium, nitrogen, argon, the well depth is going up. Again, these are the Lennard-Jones potentials for those insert gases and for the interactions between two nitrogen atoms, dispersion interaction.

All atoms and molecules have these dispersion interactions. It is just that often times the dispersion interactions can be so weak compared to some other interactions, which we are going to look at today, that we don't even think about them.

But they are actually there. But what I want to do now is to talk about what happens as we lower the temperature even further. In other words, last time we were talking about the deviation from the inert gas law as we lowered the temperature.

And what we said is that it is these dispersion interactions that are the microscopic origin for the deviation from the inert gas law which is a macroscopic law as you lower the temperature. But we also know that if you lower the temperature enough that the gas condenses, the gas liquefies.

And it is these dispersion interactions that are also responsible for the condensation of these gases. But now let's talk about, a little bit more deeply, what exactly is going on as we lower the temperature close to the liquification point.

Let me draw a Lennard-Jones potential again. And now I am going to do it for two nitrogen molecules. Here is nitrogen, here is nitrogen, two separated nitrogens as a function of r, the distance between the two nuclei.

This is our zero of interaction. And, as I said from the slide, this bond association energy measured from the bottom of the well is 0.79 kilojoules per mole, the bottom of the well were the molecules actually can never be.

But that is the well depth. Now, let's think about this. At 300 degrees kelvin, what is the average energy of the molecules? Well, the average energy is 3/2RT, as we saw. And, if I substitute in this temperature, I am going to get something on the order of 3.7 kilojoules per mole, if this has two significant figures.

3.7 kilojoules per mole. Well, let me do the following. Let me draw 3.7 kilojoules per mole here on this Lennard-Jones potential. When I do that, and I am going to start here at the bottom of the well, and I draw 3.7 kilojoules per mole, well, that is somewhere way up here compared to the interaction energy.

At 300 degrees kelvin, the bottom line is that those two nitrogen molecules have enough kinetic energy to totally ignore this interaction energy. They are way up here. If they have 3.7 kilojoules per mole of energy, they are not going to stick together.

They are not going to condense. They are actually really going to ignore this small interaction energy. They are just going to fly apart. And they do. You have a gas. However, let's lower the temperature now.

Say we lower the temperature to 100 degrees kelvin. When we do that and calculate the average energy at 100 degrees kelvin that is on the order of 1.2 or so kilojoules per mole average energy. 1.2 kilojoules per mole, we are somewhere here.

And now the relative energies between these nitrogen molecules are much lower. And it is beginning to be comparable to this well depth. And those nitrogen molecules now are deviating from the inert gas law.

They are kind of hanging around each other. They don't hit the walls as often, the walls of the vessel that they are in, because they are having an attractive interaction with their neighboring nitrogen molecule.

And so, we are deviating here from the inert gas law. The pressure is not as large if you are doing it under constant volume conditions. And then say we lower the temperature to 77 degrees kelvin, which is actually the boiling point of nitrogen to make liquid nitrogen.

Well, at 77 degrees kelvin the kinetic energy is 0.96 kilojoules per mole. And now, in this case, we are fairly comparable to the well depth here at 0.96 kilojoules per mole. What happens is the gas condenses.

The interaction energy between those two nitrogen molecules is on the order of the kinetic energy. And then these molecules stick together, the gas condenses and you have a liquid. That is the origin here of this temperature dependence and the relevance to the microscopic interactions between the molecules.

You can understand that. And then vice versa, if you start to raise the temperature, the molecules start to fly apart. They ignore this interaction. Their energy is greater than that attractive interaction.

And so what you can see in the macroscopic boiling points then is the vestiges of this microscopic interaction energy. I think I am going to put the center screen down. If you look at -- -- helium, neon, argon, krypton and xenon.

What we said is that this polarizability increases as we increase the number of electrons. We see that the well depth increases. Therefore, the boiling point increases as we go down the inert gas column.

You can see how that macroscopic boiling point is a reflection of what is happening on the microscopic scale between two individual molecules. You can also see that in this plot or in this chart. Here we have molecules, hydrogen nitrogen and oxygen.

The polarizability alpha is also increasing as we go down. Correspondingly, the well depth is increasing. Correspondingly, that boiling point is also getting larger and larger. That macroscopic quantity then reflects the change in the individual interaction energies between the molecules, the microscopic quantity.

But it also turns out that the shape of the molecules are important. For example, let's take this molecule C5 H12. There are several ways I can draw a skeletal structure for C5 H12. One way is to make it pentane, making a linear molecule.

And another way is to make this 2,2-dimethylpropane, carbon in the center, some methyl groups around that center carbon. It turns out that the boiling point of pentane is 309 degrees kelvin. The boiling point of 2,2-dimethylpropane is 283 degrees kelvin.

These are two molecules that have the same number of atoms, i.e., the same number of electrons should have the same polarizability. However, one has a higher boiling point than the other. And the reason for this is because of the different shapes of these molecules.

In the case of propane, if we have an instantaneous fluctuation in our charge distribution, it is going to be essentially along a line. That instantaneous fluctuation is essentially kind of rod-like because of the skeletal nature of the pentane.

So, one n is a little positive, one n is a little negative, the other way around. That is going to induce a dipole in a neighboring pentane molecule. And then they are going to align positive-negative here, positive negative there.

But then, in the case of dimethylpropane, you are also going to have this charge fluctuation. But in the case of propane here, this is a more spherical-looking molecule. And so, the charge fluctuation is not going to be so rod-like.

But, nevertheless, this charge fluctuation induced dipole here is going to induce another dipole in a neighboring molecule and you are going to have an attractive interaction. But, in the case of the 2,2-dimethylpropane, this is a much more spherical distribution than this.

In this case, these two dipoles are not as close together as they are in the case of pentane, meaning that the interaction energy here between the dimethylpropane is going to be less than it is in the case of the pentane.

And, again, that is reflected in the macroscopic boiling points. The boiling point of pentane is larger than that of dimethylpropane because that microscopic interaction energy is larger for propane because the induced dipoles can get closer together.

So, the shape is also important in determining these boiling points, these energies of interactions. That is going to take care of our discussion of molecules or discussion of the induced dipole ñ induced dipole interaction energy where we are talking about molecules that do not have permanent dipole moments.

But now we are going to turn to molecules with permanent dipole moments such as HCl. And, of course, in these molecules the dispersion interaction is also taking place. It is just that that is going

to be weak compared to now the interaction between two permanent dipoles.

Here we have one HCl molecule, permanent dipole. It is going to then, in a collection of HCl molecules, attract another HCl molecule. And that HCl molecule is going to align in the opposite direction.

The alignment of those two dipole is going to lower the energy. That is the attractive interaction. And then you might say you get this attractive interaction, but you also have now this repulsive interaction between the two chlorines and the two hydrogens, doesn't this all cancel out? And the answer is no.

And that is because of this. The positive end of one molecule and the negative end of the other, this distance and this distance on the opposite end are actually closer than the positive charges. The yellow distance here is smaller than the distance between the two hydrogens, is smaller than the distance between the two chlorines.

And so, it is this attractive interaction that wins out, actually. When you put those two dipoles together, the repulsion actually is there, but it is the attractive interaction that wins out and the whole system is stabilized because the distance between the unlike charges is smaller than the distance between the like charges.

Now, it also turns out that we have a functional form for the dipole-dipole attractive interaction. And that attractive interaction turns out to be a minus one over r cubed dependence. And this is exact.

You can actually derive this. You can show that this is the interaction between two permanent dipoles is one over r cubed. The quantity on the top, mu, is not a reduced mass this time. If we go back to when we started talking about dipole moments, this is the dipole moment of the molecule.

We have to use our symbols for multiple quantities. So, that is the dipole moment. We are talking about dipole-dipole attractive interactions. And that attractive interaction looks like this, minus one over r cubed.

Now, you might say where is the repulsive part of this interaction? In the case of the Lennard-Jones potential, remember we had two parts, the attractive part and the repulsive part. The repulsive part was one over r to the 12.

The attractive part was one over 4 to the 6. But it turns out that for dipole-dipole interaction we do not have a general form for the repulsive part, unlike induced dipole ñ induced dipole. So, the best we can do, in general, is to tell you that the dipole-dipole attractive interaction is one over r cubed.

But I want to compare this one over r cubed to the attractive interaction due to the induced dipole ñ induced dipole interaction. You see that the dipole-dipole interaction is what we call longer range than the induced dipole ñ induced dipole.

What I mean by that is that the value of r here, the distance between the two dipoles can be larger. In the case of a longer range interaction, it can be larger and still have some non-zero quantity for the interaction potential.

For example, if you are out here, if this value of R, you can just see with the shorter range interaction, one over r to the 6, that the attractive interaction is only the difference between the pink curve and the black curve, which is zero.

Whereas, with a longer range interaction we have more attractive interaction. This is more negative. That energy difference is larger. That is what we mean by a longer range interaction. And I want to just compare, in this diagram here, the strength of the dispersion interaction to that of the permanent dipole-dipole interaction by comparing the interaction between two argon atoms to those between two HCl molecules.

Argon only has the dispersive interaction between it because it does not have a dipole moment. And you can see that this well depth here is one kilojoule per mole, roughly speaking. But in the case of HCl that well depth here is three kilojoules per mole because that has a permanent dipole.

And, in both cases, HCl and argon-argon, we are talking about roughly the same number of electrons, not exactly but roughly, meaning the polarizability is roughly the same. The dispersion interaction energy is roughly the same for HCl as it is for argon, but the difference here is that HCl has that permanent dipole moment.

Therefore, the deeper well depth, therefore an HCl, the higher boiling point, 239 degrees kelvin as opposed to 87 kelvin for argon. What is

on this slide is just an example of how that dipole-dipole interaction energy varies with the dipole moment.

The larger the dipole, of course, the larger the interaction energy. Here I show you several molecules that all have, again, roughly the same number of atoms. They have the same mass, they roughly have the same number of electrons, so they roughly have the same polarizability.

The induced dipole ñ induced dipole is the same, but what is changing here, as I go down, is the dipole moment. For propane, dipole moment really small, 0.1 debye. Dimethyl ether 1.3. Acetaldehyde 2.7.

Acetonitrile 3.9. Dipole moment increases. The boiling point increases because that attractive interaction is increasing. It scales roughly as the dipole moment squared. The dipole-dipole interaction is stronger.

Now, I just want to briefly then remind you about one other attractive interaction that we have talked about before. And that is between two ions. There we are talking about the Coulomb interaction energy where the dependence is minus one over r.

That is the longest range interaction. Again, you can see this way out here. If I choose this value of R, the one over six interaction term would give me a very small value for the attractive interaction.

Because it is one over r to the six. You take a large number for r and raise it to the 6 power and put in the denominator. You are going to have a small value for U of r. The one over r to the three gives you some interaction energy, but one over r gives you a lot of attractive interaction.

It is the longest range. And you can also see here, in a moment, that it is going to be the strongest interaction. What I am just doing is comparing several molecules or atoms. Here is argon 2 which has only the dispersive interaction.

Here is the plot, well depth minus one kilojoule. Then there is the HCl interaction energy that has the dispersion interaction in it, but also the dipole-dipole permanent interaction. It is minus three kilojoules.

And then we are talking about chlorine 2. This is a covalent bond. This is no longer a Lennard-Jones potential energy, but this well depth here is minus 200 kilojoules per mole. And then, finally, this ionic

interaction between potassium and chlorine, look at how strong that is, minus 450 kilojoules per mole.

So, these are the relative strengths here of these interaction energies. That is all I want to say about these kinds of intermolecular interactions where we are dealing with some kind of dipole. But before we move on, I want to talk about one other kind of intermolecular interaction potential.

And that is something called hydrogen bonding. All right. A final intermolecular interaction, hydrogen bonding. Hydrogen bonding here occurs between a hydrogen atom that is attached to an electronegative atom and another molecule in the gas or in the solution.

The first requirement is that you have hydrogen attached to a very electronegative atom. Hydrogen bonding occurs for hydrogens attached to oxygen, nitrogen and chlorine. Those are all electronegative atoms.

Water is a good example. In the case of water here, hydrogen bonded to this oxygen. This oxygen is really very electronegative. What that oxygen does is it pulls those electrons away from the hydrogen.

This hydrogen is kind of partially unshielded. It is partially de-shielded. And then there is a lot of electron density here on this oxygen. Well, because that hydrogen is partially de-shielded and because it is really small, this hydrogen actually will kind of see the oxygen atoms on a neighboring water molecule.

And since this is kind of partially negative, this hydrogen will interact with one of the lone pairs on this oxygen and will form a bond. This is a little bit partially positive, this is a little bit partially negative, and the result here is a bond between the hydrogen and the oxygen.

And that bond is on the order of 20 to 60 kilojoules per mole. This bond is not a covalent bond. A covalent bond is 400 kilojoules per mole. This is 10% of it, but it is still a very important quantity or a very important phenomenon, this hydrogen bonding.

The hydrogen bonding is certainly responsible for the peculiar properties of water, as you will learn more about in 560, but it is also responsible for the unique shape often times of biological molecules.

The helix in DNA owes its structure to hydrogen bonding. The hydrogen bonding is what makes trees stand upright. The long cellulose molecules in trees are actually bonded together by hydrogen bonding.

Nylon owes its strength to hydrogen bonding. And hydrogen bonding is also responsible for whether or not you have a bad hair day. As an example of that, I want you to look at the slide up there on the walls.

What you see is a protein molecule. This is the structure of hair. The molecules that make up the strands of your hair look like this. It is a polymer. Well, it is a polypeptide. This unit right in here, carbon-oxygen bound to carbon-hydrogen bound to nitrogen-hydrogen is the peptide.

It is repeated. You see the next unit over? CO-CH-NH. CO-CH-NH. That keeps repeating. That is the repeat unit. And, of course, this carbon-hydrogen right there, you can see it has a line there indicating that it is bonded to something.

And it is bonded to something. If that carbon-hydrogen is bound to another hydrogen then you have a polypeptide which has been made from an amino acid that you might know of as glycine. If that carbon is bound to a CH3 group then that peptide was made from an amino acid that you might know of as alanine.

And if it is bound to a CH2, S, H group, well, that was an amino acid known as cystine. But what I want you to notice here is that these hydrogens on the nitrogen -- That nitrogen is an electron negative atom.

And that hydrogen, if your hair is wet, it is actually hydrogen bonded to a water molecule. Here is that hydrogen bond. And then in the next strand over, this oxygen is hydrogen bonded to a water molecule when your hair is wet.

And the bottom line is that when your hair is wet you have the strands of your hair that kind of slip by each other. There is no registry of one strand to another, because each strand has this coating here of water molecules due to hydrogen bonding.

Suppose you take your hair and put it in a very contorted configuration like this. And then you drive off the water molecules, you dry your

hair. What happens is that these water molecules then leave, the hydrogen bonds are broken.

This is not such a strong bond, 20 to 60 kilojoules per mole those hydrogen bonds are broken. And then this hydrogen on this nitrogen looks around and sees the oxygen with its lone pairs on this strand, and so you form a hydrogen bond between this strand and this strand.

And so now the strands of your hair are in registry with each other. They are actually stronger. And they do tell you not to brush your hair when it is wet because it isn't so strong. Well, it is not so strong because these water molecules are insulating each one of these strands.

And when it is dry these two strands are bond to each other. They are in registry with each other. And so, if you do this right, and you then let go of the contorted configuration, which I am having trouble doing, those strands are in registry with each other now.

And you have a good hair day. So, that is the importance of hydrogen bonding. I curled my hair just for this demo, a little asymmetric here. [LAUGHTER] But now, if you are as fortunate, or unfortunate, depending on your preference, to have naturally curly hair, then what you have are a lot of sulfur-sulfur bonds.

You have a lot of cystine peptide groups. What happens there is this. On the CH groups you have CH2 sulfur H. And on the next strand over you have S, CH2 and CH bonded to nitrogen, bonded to CO. And you actually have a covalent bond between these two sulfurs here.

This is a strong bond. The strands of your polymers in your hair are in registry all of the time. And if you want to make your natural curly hair straight you have to do drastic things like use drastic chemicals to break this sulfur-sulfur bond.

You can do it, but it is not easy. Likewise, if you have naturally straight hair and you want to curl it and make it semi-permanently curly then you have to build in the sulfur-sulfur bonds. And you have to do, again, some rather drastic chemistry to make that happen.

Hydrogen bonding is important, especially if you go to do anything in biologically- related sciences, you will see that. Now, I am going to change topics here. I am going to change topics, and we are going to talk a little bit about thermodynamics in preparation to get up to

chemical equilibrium so that Professor Cummins can come in next Wednesday and start talking about acid-base equilibrium.

He is great. You will love him. We are going to review some thermodynamics today. I am going to go kind of quickly because some of this I think you know, but I want to make sure everybody is on the same page.

First of all, bond energies. We talked about bond energies as delta E sub D. And we measured it from the bottom of the well. And I told you a few days ago I lied to you. The measured energies are really from v equals zero, and they are.

But what I am going to do is change my language. Instead of talking about energies, I am going to talk about enthalpies. I am going to talk about delta Hs rather than delta Es. The reason I am going to do this is because it is easier for us to measure a bond enthalpy than a bond energy.

And that has to do with the fact that we usually make measurements in bulk under constant pressure conditions. And that is the quantity that comes out. The relationship between delta H and delta E is this.

Delta H is equal to delta E plus delta PV. This is a relationship that you will learn about in a lot of detail in 5.60, in Chemical Thermodynamics. At this point, we are going to take it as a given.

For gases, delta H differs on the order of 1% to 2% from delta E. It is not much, but if you are doing some precise calculation you need to be aware of that. For liquids and solids, delta H and delta E are really the same for all intrinsic purposes.

The delta PV term is really very small. And, in thermodynamics, since we are most always looking at changes in energy, we need what we call standard states. And we are going to put a knot here on all of our delta Hs to designate the standard state.

And our standard state that your book uses, and will use, refers really the pressure. And the pressure is one bar. And one bar is equal to 10 to the 5 Pascal. That is equal to 10 to the 5 kilograms per meter second squared.

The delta Hs we are going to talk about are also, just about all of them, measured at 298.15 degrees kelvin. Delta H does depend on

temperature, but we actually are not going to look at that in the next few days.

You are going to do that in 5.60. Our delta Hs are going to be delta Hs at 298.15 degrees kelvin. On the first slide here, I show you a bunch of bond enthalpies for CH bonds. And, of course, those bond enthalpies are a little bit different, depending on what molecule you have.

But they are not that different. And so, what is often done, and your book does this, is that somebody goes and calculates the average of the bond energies for lots of CH bonds and lots of molecules and prepares a table that looks like this.

This is the mean bond enthalpy. And they have CH, CC, carbon-carbon. But these are average bond enthalpies. Now, why are bond enthalpies important to us? Well, they are important because they determine the enthalpy of a chemical reaction.

If the bonds are stronger in the products than in the reactants that is going to give us an exothermic reaction. If the bonds are stronger in the reactants than the products that gives us an endothermic reaction.

And so let's look at this reaction. This is an important reaction. This is the oxidation of glucose. This is a reaction very exothermic, minus 2816 kilojoules per mole. It is a reaction that is being carried out in every cell of your body as we speak.

It is the reaction that is providing the energy to maintain your body temperature, the energy to move your muscles, the energy to repair tissue and the energy to think. Important reaction. This is the reason why we eat.

This is the reason why we breathe, this is the reason why we exhale and this is the reason why we pee. [LAUGHTER] What do we need to do here to calculate the enthalpy for this reaction? We have to figure out how much energy is required to break all of the bonds of the reactants because that is how much energy we put in.

And then we have to figure out then how much energy we get back when we form the product bonds. Bottom line is the enthalpy necessary to break all of the bonds, you can calculate, is 12,452 kilojoules per mole.

That number comes from using these average bond energies I told you about. We can then get back some energy minus 15,000 approximately when we form some new bonds. That number comes from those average bond enthalpies.

The difference between these two energy levels is the exothermicity of the reaction. Now, what did we do to get the enthalpy? Well, what I did is took the bond enthalpies of each bond of the reactants and summed them.

Then I took the bond enthalpies for each one of the products, summed them and subtracted the two to get the enthalpy of the reaction. I want you to notice something here important. This is reactants minus products.

In a moment, I am going to show you another way to calculate the enthalpy for a reaction. And it is going to be products minus reactants. You have to know this. But you also see that the calculated enthalpy is not the experimental enthalpy.

Why? Because we use the average bond enthalpies. We did not use the exact bond enthalpies because if we had to use the exact bond enthalpies, can you imagine the size of the table of data that we would have to have? We would have to have a bond enthalpy for every known molecule.

That is a lot. What are we going to do then? Is there a more accurate way to do that? Yes, with knowing the absolute bond enthalpies. But that is too much data. Is there some other way to do it? Yes.

We are going to use heats of formation. A heat of formation, delta H knot with an F as a subscript. The heat of formation is the enthalpy of a reaction that forms one mole of a compound from the pure elements in their most stable form in their standard state.

For example, here is water. We are forming one mole of water from its elements, hydrogen and oxygen. The enthalpy for this reaction is defined as the heat of formation of water. Why is this the heat of formation of water? Well, because we are forming one mole, and that is important, from the elements that make up water.

What elements are they? They are hydrogen. But notice that this hydrogen is H2. It is not hydrogen atoms because H2 is the most

stable form of hydrogen. Oxygen is O2, not oxygen atoms because this is the most stable form of oxygen at bar pressure.

Look at this here. What is the heat of formation of oxygen? Well, the enthalpy change for this reaction is zero. That is the heat of formation of oxygen. Why? Because we are forming one mole of oxygen from the elements in their most stable form.

For elements like oxygen, hydrogen, nitrogen, chlorine 2 in the gas phase, those all have heats of formation that are equal to zero. And then, finally, here is the expression or the reaction that gives us one mole of glucose.

The enthalpy for this reaction is the heat of formation of glucose. We get it from its elements, hydrogen, oxygen, and look at the elemental form, the most stable form of the element carbon is graphite.

Is there an 18.0-something exam? Yes? OK. See you on Monday.