Concepts of Chemistry for Engineering
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Lecture 64
Real gases - Part 2

Hello, everyone, welcome to the module where we are discussing intermolecular forces, and its impact on the properties of systems. We are going to continue our discussion on the impact of intermolecular forces on real gases. And in this lecture, we shall look at what are called as van der Waals equation and what are the different properties and what are the different caveats of it. Before we get into it, let us just refresh our memories on what we discussed in the last lecture.

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In the last lecture, first we had looked at what is the influence of intermolecular interactions on the properties of real gases. We had seen that there are two aspects to the interaction that is one is the attractive force that is when you bring in two molecule through a far distance close to one another, there is invariably an attraction.

But if you push the molecules even further then the repulsive interaction would kick in and that would lead to sort of an excluded volume effect. And this has important consequences in the way the actually the gases behave, that is, how they liquefy and their behavior with respect to temperature, pressure and volume.

So, in this context, we had seen a term called as a compression factor, which is basically nothing but a ratio of the molar volume of a real gas to that of an ideal gas. And we had seen that this factor or the compression factors Z also depends heavily on the intermolecular

interactions, that is, it is not a flatline as it is for a ideal gas, it has its own curvatures which again capture the attractive and the repulsive part of the interaction between molecules.

And taking this discussion further, we had looked at what is called as an virial equation of state where the idea was to start with an ideal gas equation and modify it in such a way that one could take into account the real part or the interaction between the molecules into account and this is what we ended up with the virial equation. And we are told that the virial coefficients that is B and C are two dependent temperature.

However, we are mostly interested in the second virial coefficient or the second virial second till the second term, because third and the higher order terms are generally negligible in their contribution to the pressure. So, with this, we shall now try and look at another formalism to understand real gases which is called as van der Waals equation of state. And let us begin by looking at this van der Waals equation of state. So, in order to understand this, let us start again from the ideal gas equation and see how do we get to this van der Waals equation from an ideal gas equation.

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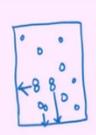
So, again we start with PV is equal to nRT, and this is for an ideal gas. And we know that for a real gas it has two components, one is attractive interactions, attractive forces and the other is the repulsive part. So, now, having understood or having known these two, let us see if we can now try to understand or try to modify the ideal gas equation so as to capture both the attractive as well as the repulsive parts.

So, I am going to write the in terms of P that is P is equal to nRT divided by V. And on this side, I am going to draw a box, which has gas molecules, which are shown by these beads. And let us call the volume of this container as V, and now you have different gas molecules around it. So, now, if I were to understand the pressure of this particular let us say a real system that is a gas let us say have a methane or ethane contained in a particular in a container, so then, let us see what do I look at. So, now, I have the ideal gas equation.

However, we do know that the volume or the let us say molecules of methane or ethane do have a finite volume. So, they are not, their volume is not negligible or 0, they do have a finite volume. So that means, this equation, the ideal gas equation from that, I should subtract some part of the volume which is occupied by the molecules of ethane, methane or any of the molecule to get towards a real situation. So, for that, I will write minus some factor. So, that would correct my volume part.

Now, coming to the pressure. So, if I have to actually capture the real pressure of a real gas molecules such as methane or ethane, I should now start taking into account the attractive or repulsive parts. So, now let us see what happens with these attractive or repulsive parts. So, with this, there are two things which happen.

One is that, if I actually have, if the molecules actually come together, then they would attract with one another. If let us say if these molecules are now coming together or if they are forming an attract, if they are having undergoing an association, then the force and the frequency with which they impinge on the walls, that is, this would decrease compared to them being free.

So, that means, the attractive interaction between the two molecules actually reduces the force, as well as, the frequency with which the gas molecules impinge on its walls. So, again, repeat it, the attractive part of the interaction means that I will no longer be able to hit the walls of the gas molecule with the same frequency as well as a force if it were a ideal gas because now the some of the molecules are actually held together and they have formed a small complex or cluster. So, that means, the pressure which will exert on the walls of a of this container be lesser than it were for ideal gas.

So, that means, I need to subtract this by some term. Let us leave this blank for the time being, but I need to subtract. I hope, this logic is at least clear to everyone that the volume would be the actual volume, which is available for the molecules to move around would be

less than the ideal volume because the gas molecules do have a finite volume that is methane, ethane or other molecules.

And if you try to actually push one into another, you would end up into the repulsive interactions. And this repulsive interaction means, the actual volume is actually less than what it were for ideal gas. That is point number one. And coming to the pressure term, what we see is that the pressure exerted by a real gas on the walls of a container is also lower than if it were ideal gas. And this is because of two reasons, that is, one is the force and the second one is the frequency.

Frequency of impingement of gas molecules on the walls of a container. So, these, both these factors that is force and the frequency get influenced if the molecules associate with one another and form a small clusters or small kind of complexes. So, having understood that, the repulsive part would lead to a reduction in the actual volume available for the gas molecule. And the attractive part let us just write it here, this comes because of the attractive interaction, and this comes because of the repulsive part or the repulsive forces, which forces the volume cannot be 0, you will have the finite volume for the gas molecules.

So, having understood this by general arguments, now let us try to go ahead and put some numbers or put some actual values for this. So, what people typically write is, that P is equal to nRT divided by V minus n times b, b is a factor, which actually captures the repulsion between the molecules or it is actually nb is together is what can be regarded as the volume occupied by the gas molecules, and minus a. And coming to this part, the attractive part let us look at these two terms that is the force and the frequency.

So, what do these two terms depend on? That is the force and the frequency. So, I hope you agree or you at least see that it makes sense to say that these two quantities that is the force and the frequency are directly proportional to the molar volume, to the molar concentration or the number of molecules per unit volume.

In other words, it is n divided by V. Because, if you have more number of molecules then their frequency of collision would also be more and the force would also be higher, and as a result, these two quantities that is force and the frequency are directly proportional to the molar concentration of the gas molecules.

So, now, what we can do is, since these are two terms which are interacting, so, the net effect will be the square of it. So, I will put a proportional to the constant a times n squared by V

square. So, this entire thing can be written in a slightly different form that is P is equal to RT divided by Vm minus b minus a divided by Vm square.

So, I have just divided both numerator and denominator by n and that would give me this particular expression. That is P pressure of a real gas is equal to RT divided by the molar volume minus a term called as minus a factor called as b which is a constant for a given gas and this whole thing minus a which is again a constant for a given gas divided by the molar volume square.

So, this is what is called as the van der Waals equation of state and a and b are the van der Waals constants, van der Waals coefficients or van der Waals constant for a given particular gas and what these indicate is b indicates the repulsion or the extent of repulsion and a indicates the kind of a measure for the attractiveness for particular gas. And these are actually constants for a given gas and they do not invariably depend on temperature.

So, a point which is important to be noted here is that this equation or this kind of an argument was given by Johannes van der Waals in about 1875. And he did not give a rigorous proof of this expression. He took the ideal gas expression or the he took the ideal gas arguments and then he said, let us say that the molecules have an attractive interaction, because if you bring them close together, they have the induced dipole, induced dipole interaction and if you bring them even further than they would have a repulsive interaction. So, they have a volume which you cannot occupy that is the molar volume of a given gas or the volume of a given gas molecule.

So, with these two simple arguments, he came up with this kind of equation of state. And this equation of state has actually stood the test of time and it is a very nice way to phenomenologically explain the behavior of real gases. So, I hope, you appreciate that. You do not have to mug up or you do not have to remember anything. As long as you remember that how gas molecules interact with one another.

Again, going back to our previous analogy of gas molecules being similar to human beings, if you bring, if they are all separated well, well separated, then there would be no interaction among them or minimal interaction among them. But the moment you try to bring molecules or people together they would interact with one another. And that is what would result in this or would result in the deviation from the ideality and van der Waals has captured this by using phenomenological arguments rather than a rigorous mathematical proof, which is very important to note.

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Real gas and its characteristics

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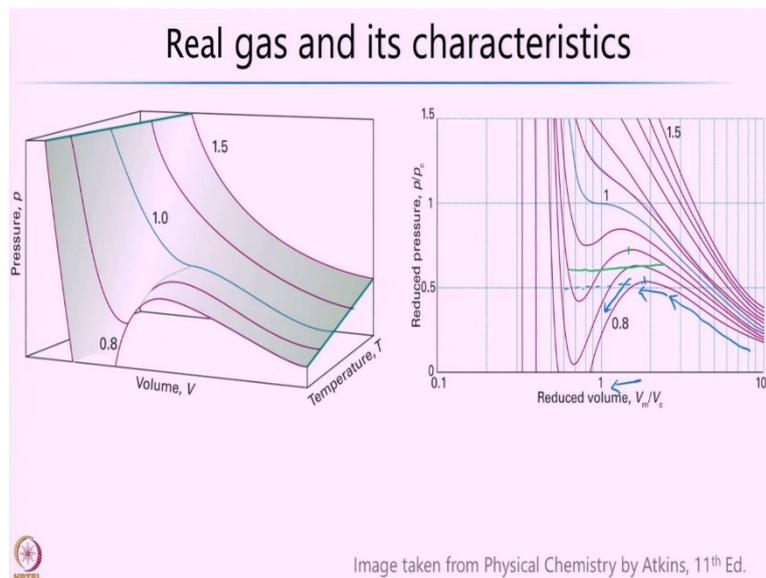
So, having seen the simple equation of state or the van der Waals equation of state now let us go ahead and look at how does the occur or what is the nature of this curve. So, for that, what is done here is, here is a plot or a three-dimensional plot of a pressure, volume and temperature.

So, you could, for the time being, you could just look at one of the temperature curves and neglect the others. And what you see is that if you start looking at this temperature curve, it goes up and then sort of comes down and then finally, you do not see it here because it is cut off and then it finally again comes up, and the same thing you see as you go further higher now the next curse as well.

So, if you now take a two-dimensional cross section of these isotherms then, one would get a graph which would look something like this. And if you remember from a previous lecture, we had said that, that initially you would, the molecules would behave similar to ideal gas until a certain reduction in the volume, but beyond a certain reduction, they would actually sort of undergo a liquefaction because of the attractive forces between them, and that would result in a flatline. And finally, once you have all the liquid and if you try to again further reduce the volume that would lead to a repulsion because you cannot compress the liquid beyond a certain point.

So, that is the picture what we had in the last lecture, if we now look at this particular let us say the P versus V diagram, which you get out of van der Waals equation, it looks slightly different. So, you again start at a higher volume, you keep decreasing the volume, and then the pressure goes up, which is normal. And then, at a certain juncture, it actually as you

reduce the volume, the pressure actually goes down, and then it comes up, which is a bit of an anomaly.

So, I will just try and point that out to you, so to make it more clear. So, if we try and take a look at this particular graph, we have come, here the volume has been reduced starting from the here till here. So, you still keep reducing the volume, the pressure goes up. But from here and beyond, what you do is, as you reduce the volume, you also see a drop in the pressure, which is actually counterintuitive, or you do not expect that. So, this is where actually the van der Waals equation of the state does not capture the real behavior completely well, that it has a deviation from the what one would expect for a real gas, because if it were real gas, you would expect it to be remain constant something like this.

However, here the van der Waals equation predicts a drop in the pressure with a decrease in the volume, which is counterintuitive. To rectify this people have come up with what are called as Maxwell's lines or they have just drawn some horizontal lines, such that let us say if I take this particular curve here, I will use a different ink now.

Say, if I take this particular curve, so what people have done is they draw a horizontal line here. So that an equal portion is above the curve and an equal portion is below, so as to sort of nullify the whole effect which the van der Waals equation predicts. So, this is a bit of an unrealistic or unphysical, or a situation which does not take place in the real world with real gases that is a drop in the pressure with decreasing volume. So, to account for that, you draw these kinds of lines which are called as Maxwell's lines. And this is used to do a correction to the van der Waals equation. So, now, let us go ahead and try to look at what are the main characteristic features of this van der Waals equation.

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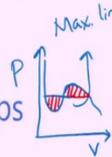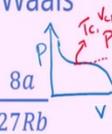
So, I will again, rewrite the van der Waals equation, so that, we all remember what we are talking about. That is, the P is equal to RT divided by Vm minus b minus a divided by Vm square. So, I hope everyone remembers this. And once we have this particular equation, so then the following features become pretty obvious that is, the first one is at high temperature at a very large molar volume, then the equation should or equation tend towards an ideal gas.

That is, let us say, if I have the temperature term, which is pretty high, that means this term, the first term would be very high. And if the molar volume Vm is also very, very high, or we are looking at a very large volume, then, the second term actually becomes vanishingly small compared to the first. So, then this equation would tend towards P is equal to RT divided by Vm with the b factor being very small in comparison to Vm.

That is, if Vm is much, much bigger than b, that is what we are talking about that Vm is very, very large. So, in other words, the van der Waals equation of state can actually be also be used to describe in the limiting cases the ideal gas equation that is when the temperature is very high and the molar volume is also very large.

And the second important feature of the van der Waals equation is, it shows the existence of the liquids and the gases in what are called as van der Waals loops or if you just to refresh your memories I hope you remember in this I will just draw a small curve here, volume versus P, we had this kind of curves and we had called them as Maxwell's lines, these is Maxwell line, Maxwell line and these are what are called as the these are what are called as van der Waals loops.

So, these loops actually predict or at least tell us about the coexistence of gas and liquid. So, this is very similar to what we saw even for the, even in the last lecture where going till the, if you remember the letters we had going from C to E there was a complete liquefaction which was taking place from E onwards the liquid was incompressible, so you had a huge rise in the pressure. So, this is very similar to that.

And the third and the most important the point is that the van der Waals equation of state can also be used to derive what are called as critical constants, in terms of the van der Waals' coefficients. So, I will just try and explain that to you in a minute. So, if you again take this particular kind of an expression or let me try and draw it here a small one.

So, if you have a point where actually the, if you have along the P V curve a point where actually you do not have the or the liquid and the gases coexistent line actually coincide or they become, they merge into a single point and then it goes up then this one would call it as a critical point or the Tc or the volume as Vc and the pressure as Pc. The corresponding component that is the temperature pressure and the volume are called as critical temperature, critical volume and critical pressure.

So, at this let us say at this line, if you now take the derivative and the double derivative, they should both equate to 0. And if you use, just use that this mathematical statement that is at this critical temperature and pressure and volume, the van der Waals equation states or the first and the second derivative of van der Waals equation can be equated to 0 then just by doing a bit of algebra, you can end up on these terms that is the Vc and the Pc and the Tc in terms of the van der Waals coefficients that is a, b and the universal gas constant r.

So, this is a very useful way to actually calculate the critical constant for a given gas and also to actually check back or to go back and look at the van der Waals coefficient which you obtain for a given system are they actually correct based on the experimental measurement of the critical constant that is temperature, pressure and volume.

So, now, we have looked at what are the different features of the van der Waals equation of state, and we also talked a bit about the critical temperatures in the critical volumes. So, now let us go ahead and look at this in a little more detail. What are these critical temperatures, pressure and volume mean?
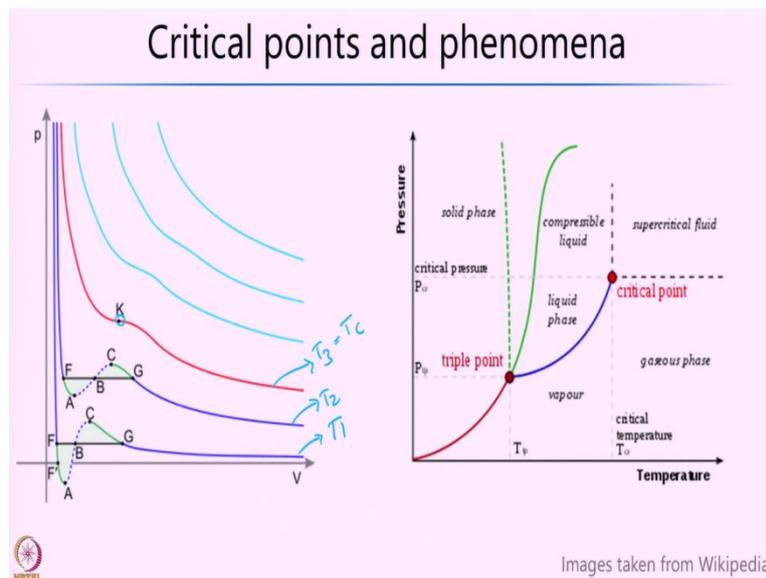
So, to understand that, again, let us go back to the pressure volume graphs. So, I hope, you remember that we start at a very high volume, and then as we start compressing then the, at a certain point, you at around point G you have a liquefaction which starts taking place, and that continues till F. And so from there on the liquid becomes incompressible. And in between the G and F you always have a coexistence of the gas and the liquid. And this is what I tried to draw in the previous graph where you have what van der Waals equation predicts are these dotted lines and the shaded areas are called as van der Waals loops.

So, if you now keep on changing the temperature, that is, if you keep on recording that at various temperatures because these are isotherms so this is at let us say T1 and this is at T2 and this is at say T3. And you see a point where these two the G and the F actually come back and merge to this K. And this is the point which is called as a Tc where both the liquefaction is completed the single point, and this is what is called as a critical temperature and the corresponding pressure and the volume are called as the critical pressure and the critical volume.

And this can be represented in a slightly different way in what are called as PT phase diagrams or a pressure and temperature phase diagrams, where you have a temperature on the x axis. And let us just try and look at this part that is you have vapor and a liquid phase because that is what we are trying to do. You go from a gas or the vapor phase to the liquid phase and what you see is that beyond a certain point, you have what is called as critical point and here and beyond, beyond this pressure and temperature here what is one call it as a supercritical fluid or a state in which the properties of the system are in between those of a

liquid and a gas. And so, you must be wondering what is this sort of enigmatic term he is calling it as a supercritical fluid.

So, the main idea of the importance is that the properties of this particular state, which is called a supercritical fluid, are somewhere in between those of a pure liquid and a pure gas. So, what that means is that you can actually have a, you can make use of both the properties and you use it in some sort of an application. To give you a feel for the applications, if you think of carbon dioxide, and if you take a look at the critical temperature and pressures of carbon dioxide the critical temperature is around 31 degrees C, and the critical pressure is about 72 atmosphere.

So, by now varying the pressure, you can go to its critical supercritical fluid phase. And in the supercritical fluid phase, you have entirely different properties. And the properties are they have very different solubilities, they have very different let us say densities, and this can be made use to extract different materials in a mixture.

For example, if you have a coffee-beads, and if you are trying to extract caffeine out of it, actually, using the supercritical carbon dioxide is a very, very benign and a sustainable way to actually extract caffeine out of the coffee beans. And also, by just playing around with the pressure, one can selectively extract different components.

So, that is the reason why a lot of technological importance and relevance is given to supercritical fluids. And I hope, this convinces you or at least gives you a flavor of why one should study the supercritical phenomena or the supercritical fluids. So, with this, we shall stop our discussion here. And in the next class, we shall look at potential energy diagrams and what do they tell us about bonding in molecular systems. Thank you.