Chemical Principles 2
Professor Dr. Arnab Mukherjee
Department of Chemistry
Indian Institute of Science Education and Research, Pune
Van der Waals Gas

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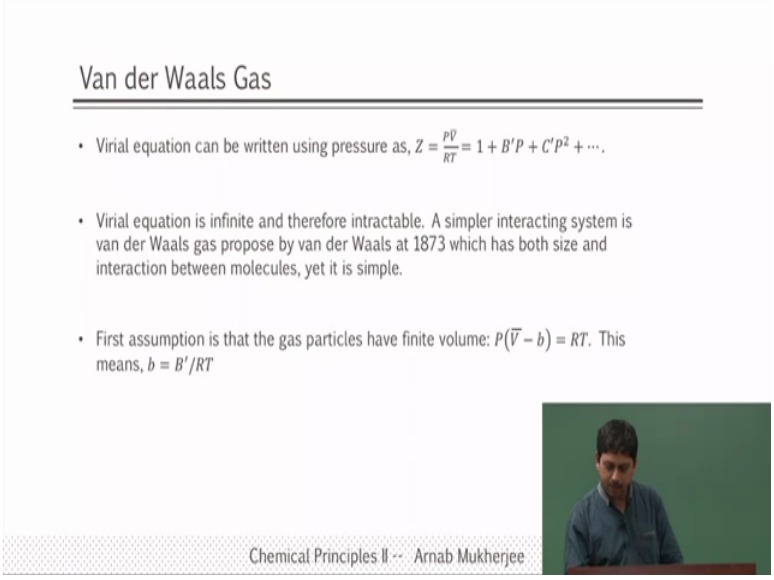

Van der Waals Gas

- Virial equation can be written using pressure as, $Z = \frac{P\bar{V}}{RT} = 1 + B'P + C'P^2 + \cdots$.
- Virial equation is infinite and therefore intractable. A simpler interacting system is van der Waals gas propose by van der Waals at 1873 which has both size and interaction between molecules, yet it is simple.
- First assumption is that the gas particles have finite volume: $P(\bar{V} - b) = RT$. This means, $b = B'/RT$

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So as I said that real gas is more complicated because it is like an infinite series, right we need several possible several coefficients in order to express the profile the variation of the compressibility with pressure or volume. A simpler interacting system was proposed by Van der Waals in 1873 actually before the real gas real expression came is proposed by Van der Waals. To understand that how an interacting gas molecules would look like?

So what will be the equation of state for a simpler interacting system not as complicated as real gas, neither as simple as an ideal gas somewhat in between a compromise.

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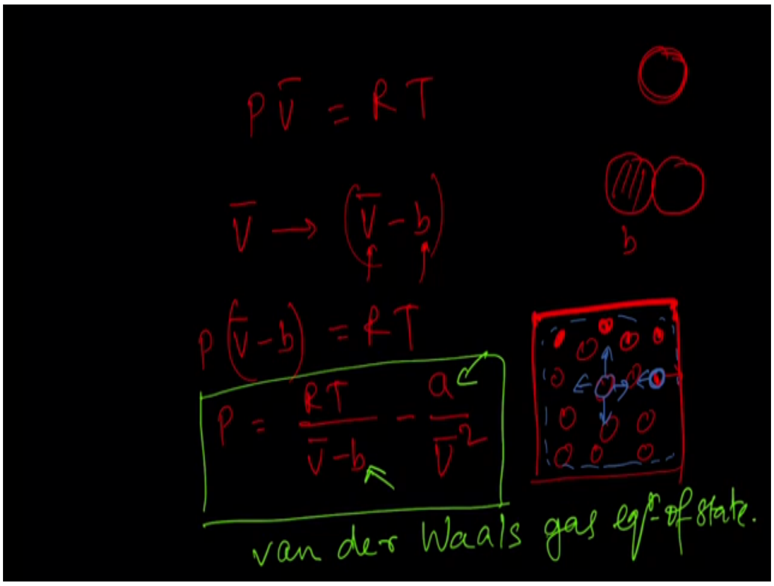

So the compromise is done this way that the first assumption is that we have PV equal to RT, right this is with the condition that there is no interaction between the particles and therefore two particles can even overlap on top of each other. However, let us say we say that the particles cannot overlap on top of each other, so they can be as close as you know touching each other.

So in that case one has to consider the volume b of the particles now then overall volume of the system will become V to V minus b so this is a molar volume this is molar volume of the particles alone and this is molar volume of the system. So then our equation goes to PV minus b equal to RT. Now we rearrange this we rearrange by P equal to RT by V minus b, so this is one part of the correction from ideal gas that we use a finite size of the particles finite volume of the particles.

So imagine all the particles are touching each other, we will be able to calculate the overall volume and that will be the volume of b actually it is not quite let us say volume of one particle is x then there are n number of particles it will be xn that xn is equal to b even they touch each other there will be interstitial spaces and all that, so therefore it is not equal that is why I said it is not equal so anyway once we have the volume we can derive that.

Now second correction would be that if there is interaction amongst the particles so this is assuming no interaction, right it is only assuming that they are like hard sphere like two marbles they cannot be on top of each other even if you bring them it will be as close as touching each other, right that is called hard sphere, but let us say you say that no they also have interaction it is not just their size, they are also interacting with each other, which means they are having an attractive iteration.

So in that case what is going to happen is that imagine a box of full of molecules, now how does this molecule put pressure on the wall? It put pressure because it goes (to) and hits the wall it gives force on the wall and force by area is the pressure. Now if there is interaction between the particles then this particle which is on the close to the wall will be pulled inside by the other particles, the particles which is inside there is force pulling it from all sides.

However, the particles which are on the surface there is some asymmetric force coming out from the inner molecules which is pulling them towards it in an attractive manner, what will happen in that case? Will the pressure be more or less on the wall? Less, so that less pressure is formulated as a by V square, so why it is V square because on one particle there are there is a you know all other particles which is attracting towards it, so therefore it goes as 1 by V square.

So now we have this particular equation of state which is called Van der Waals gas equation of state. Why it is so good? Because it gives you a feel of real gas, but much less complicated way and it is tractable you know that b is the size and you know a is the attractive iteration, so given a and b we will be able to actually understand a change the behaviour of this particle.

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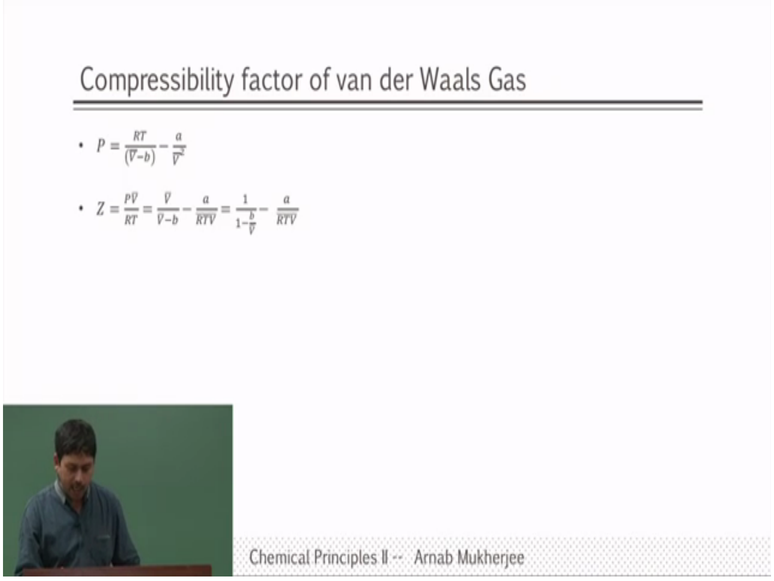

Compressibility factor of van der Waals Gas

- $P = \frac{RT}{(\bar{V}-b)} - \frac{a}{\bar{V}^2}$
- $Z = \frac{P\bar{V}}{RT} = \frac{\bar{V}}{\bar{V}-b} - \frac{a}{RT\bar{V}} = \frac{1}{1-\frac{b}{\bar{V}}} - \frac{a}{RT\bar{V}}$

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Now how do we calculate now the compressibility factor? So this is equation of state.

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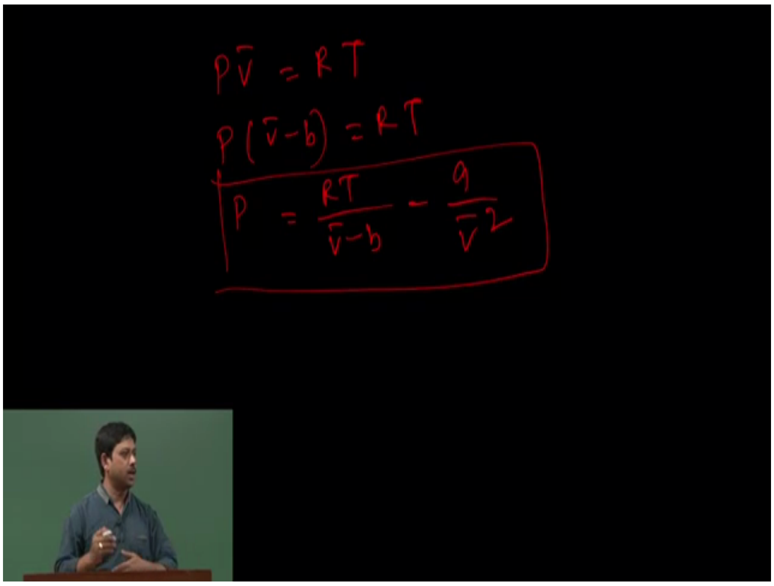

$$P\bar{V} = RT$$

$$P(\bar{V}-b) = RT$$

$$\boxed{P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}}$$

Now let us say we try to write compressibility factor so I can actually do that again that is the simple derivation PV equal to RT, now P V minus b is equal to RT and then we get P equal to RT by V minus b minus a by V square, so this is our Van der Waals equation of state, okay because we do not have to remember that we can always start from ideal gas and come to that.

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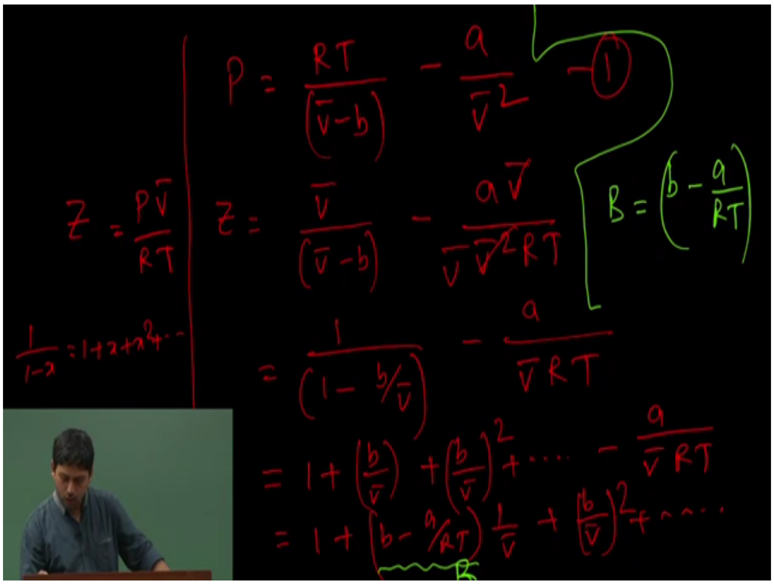

$$P = \frac{RT}{(\bar{V}-b)} - \frac{a}{\bar{V}^2} \quad ①$$

$$Z = \frac{P\bar{V}}{RT}$$

$$\frac{1}{1-x} = 1 + x + x^2 \cdots$$

$$Z = \frac{\bar{V}}{(\bar{V}-b)} - \frac{a\bar{V}}{\cancel{\bar{V}}\bar{V}^2 RT}$$

$$B = \left(b - \frac{a}{RT}\right)$$

$$= \frac{1}{(1 - b/\bar{V})} - \frac{a}{\bar{V}RT}$$

$$= 1 + \left(\frac{b}{\bar{V}}\right) + \left(\frac{b}{\bar{V}}\right)^2 + \cdots - \frac{a}{\bar{V}RT}$$

$$= 1 + \underbrace{\left(b - a/RT\right)}_{B}\frac{1}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \cdots$$

So P equal to RT by V minus b minus a by V square, so that is the Van der Waals equation of state, right. So now we have to calculate Z, which is PV by RT. So therefore, in the case of this particular equation equation number 1 I can multiply by V and I can divide by RT, so multiplying by V and dividing by RT what I am going to get is V bar by V minus b minus multiplying by V and dividing by RT, going to get this, so this is now the compressibility factor we will simplify it, divide by V in the numerator and denominator here, so 1 by 1 minus b by V bar minus a 1 will cancel by V RT.

So now we will have to use one trick is that we know that 1 by 1 minus x can be written as 1 plus x plus x square and things like that, right so we are going to use that series how our x here is b by V. So let us write that 1 plus x which is b by V plus b by V square plus dot dot dot minus a by V RT which is 1 plus now I have the V common so b minus a by RT multiplied by 1 by V plus b by V square and higher order.

So now we have written the compressibility factor in terms of the series that we were writing for real gases, right. So now do you identify the B here, so this is our b (I cannot write here) so our B here is b minus a by RT, okay. So what does it mean? So it gives us a you know a lot of information, first of all we can always neglect anything higher order second order or higher, we can always truncate it at the first order which is 1 plus b minus a by RT into V.

Now you can see here is that so we have alreandy taken minus of a so a negative value of b indicates basically positive value of a that is how that. So whenever the term a by RT is larger than b we are going to get a negative b and we are going to see a dip, right. So let us say what will happen at low temperature?

At low temperature this a by RT quantity is going to dominate because temperature is in denominator so the lower value a by RT will be higher and therefore this term b minus a by RT will dominate and therefore it will become negative, therefore you see that at lower temperature it was going down, but at a higher temperature a by RT can be neglected and you simply have 1 plus b by V and b being positive quantity because it is a volume it is going to always be positive larger than 1 and that is what I saw in the real gases, right?

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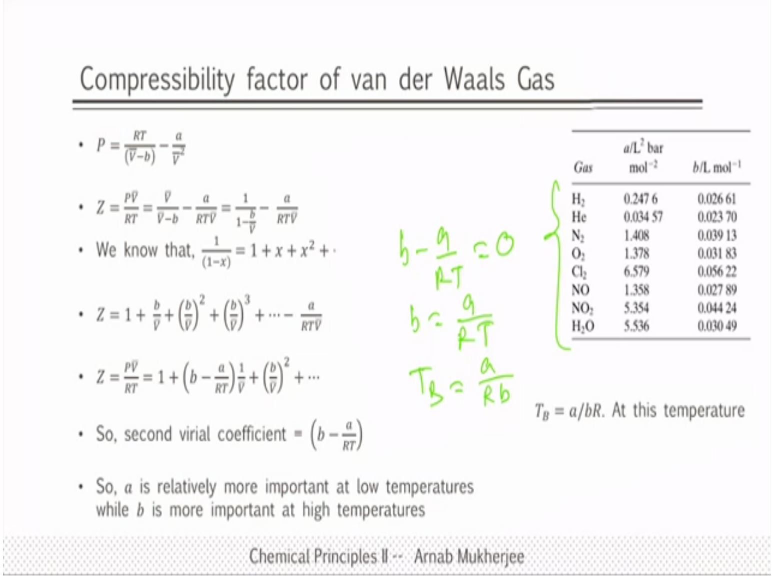

Compressibility factor of van der Waals Gas

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- $Z = \frac{P\bar{V}}{RT} = \frac{\bar{V}}{\bar{V}-b} - \frac{a}{RT\bar{V}} = \frac{1}{1-\frac{b}{\bar{V}}} - \frac{a}{RT\bar{V}}$
- We know that, $\frac{1}{(1-x)} = 1 + x + x^2 + \cdot$
- $Z = 1 + \frac{b}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \left(\frac{b}{\bar{V}}\right)^3 + \cdots - \frac{a}{RT\bar{V}}$
- $Z = \frac{P\bar{V}}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \cdots$
- So, second virial coefficient = $\left(b - \frac{a}{RT}\right)$
- So, a is relatively more important at low temperatures while b is more important at high temperatures

$b - \frac{a}{RT} = 0$

$b = \frac{a}{RT}$

$T_B = \frac{a}{Rb}$

Gas	a/L^2 bar mol^{-2}	b/L mol^{-1}
H_2	0.247 6	0.026 61
He	0.034 57	0.023 70
N_2	1.408	0.039 13
O_2	1.378	0.031 83
Cl_2	6.579	0.056 22
NO	1.358	0.027 89
NO_2	5.354	0.044 24
H_2O	5.536	0.030 49

$T_B = a/bR$. At this temperature

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So b minus a by RT so let us see if I have that. So this derivation is exactly here which we have just now done. So second virial coefficient b is given here which I have done, a is therefore relatively more important at low temperature and b is relatively important at high temperature because at high temperature a by RT term is going to be neglected, so therefore b is more important than that value.

And here so now the thing is that Van der Waals gas is not a real gas. However, we can use this Van der Waals equation to fit atleast smaller regions of the volume variation and that we can arrive at certain values of a and b and you can see those values are here and we can also calculate the boyle's temperature where b minus a by RT is 0, so simply b equal to a by RT and therefore T B which is boyle's temperature is a by RT, okay.

We want to show you how with the two parameters a and b the equation of state changes, so for that we are using some software called Mathematica in which one can plot both 2 dimensional and 3 dimensional pictures profiles and with that we can show you how as a function of a and b the quantity changes.

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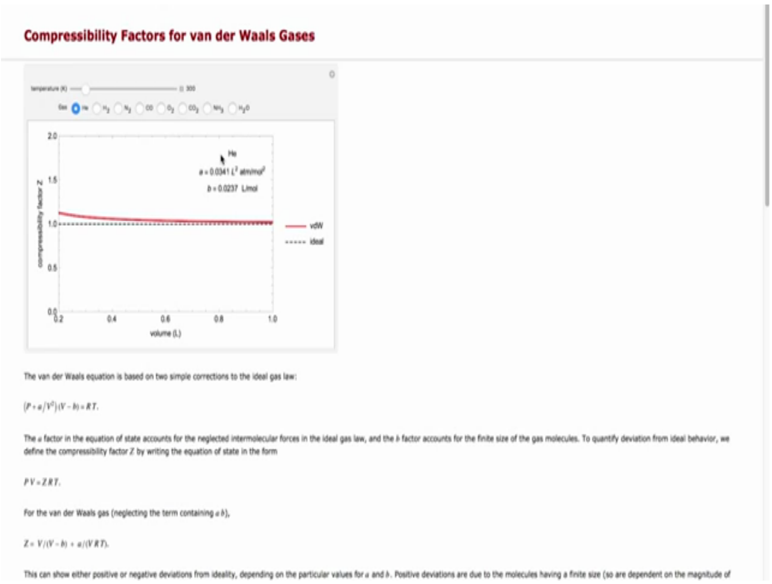

Compressibility Factors for van der Waals Gases

The van der Waals equation is based on two simple corrections to the ideal gas law:

$(P + a/V^2)(V - b) = RT.$

The a factor in the equation of state accounts for the neglected intermolecular forces in the ideal gas law, and the b factor accounts for the finite size of the gas molecules. To quantify deviation from ideal behavior, we define the compressibility factor Z by writing the equation of state in the form

$PV = ZRT.$

For the van der Waals gas (neglecting the term containing $a\,b$),

$Z = V/(V - b) + a/(VRT).$

This can show either positive or negative deviations from ideality, depending on the particular values for a and b. Positive deviations are due to the molecules having a finite size (so are dependent on the magnitude of

So just to give you a brief intro to mathematica, are you familiar with mathematica software? Okay, so you know remember that we do there are different softwares like programming softwares where we can write programs from for numerical problems, right we can do differentiation, integrations and get numbers. Mathematica is once a software where you can do analytical calculations which means that you can do differentiation, integrations and lot more different mathematical task using this particular software.

It is so good that even mathematicians use it regularly. You can plot 2 dimensional and 3 dimensional figures in this and it is extremely useful, not only that it is also you know there are lot of demonstrations available to understand a particular concept, let us say you have a complicated function and you want to see how it behaves, you can plot that in mathematica and see that.

So you saw that our you know equation Van der Waals gas equation was slightly complicated, right so one can plot and see how it behaves as a function of both those two parameters a and b.

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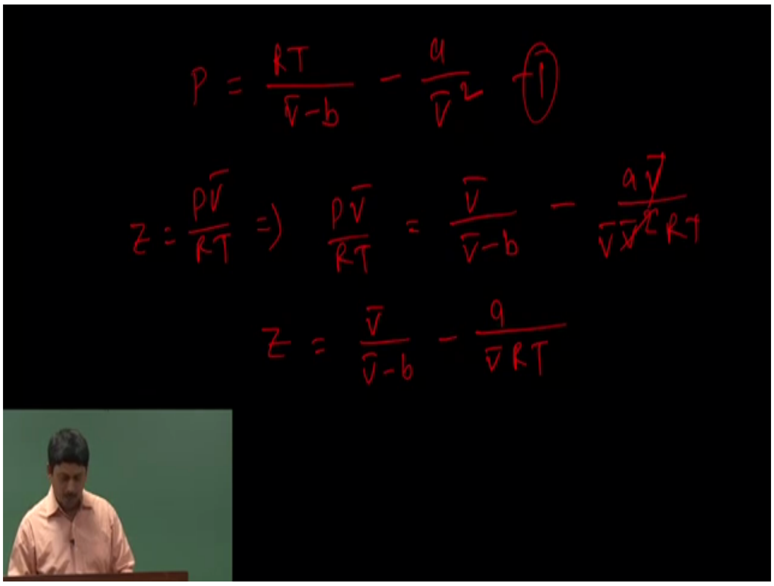

$$P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2} \quad ①$$

$$Z = \frac{P\bar{V}}{RT} \Rightarrow \frac{P\bar{V}}{RT} = \frac{\bar{V}}{\bar{V}-b} - \frac{a\bar{V}}{\bar{V}\cancel{\bar{V}}^{2}RT}$$

$$Z = \frac{\bar{V}}{\bar{V}-b} - \frac{a}{\bar{V}RT}$$

So if I remind you the equation was P equal to RT by V minus b minus a by V square that is the Van der Waals equation of state, right. So now if I have to plot this quantity, so we have to express the quantity Z which is PV by RT, right so we have to so this is Z is compressibility factor PV by RT, right. So that means if I now multiply PV by RT on both sides of this equation 1, I am going to get V by V minus b minus I am multiplying with V and dividing by RT, so this cancels and I get V, so Z becomes V by V minus b minus a by V RT.

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The van der Waals equation is based on two simple corrections to the ideal gas law:

$(P + a/V^2)(V - b) = RT.$

The a factor in the equation of state accounts for the neglected intermolecular forces in the ideal gas law, and the b factor accounts for the finite size of the gas molecules. To quantify deviation from ideal behavior, we define the compressibility factor Z by writing the equation of state in the form

$PV = ZRT.$

For the van der Waals gas (neglecting the term containing $a\,b$),

$Z = V/(V - b) - a/(VRT).$

This can show either positive or negative deviations from ideality, depending on the particular values for a and b. Positive deviations are due to the molecules having a finite size (so are dependent on the magnitude of b) and negative deviations are a result of the intermolecular forces (so are dependent on the magnitude of a).

If a and b are zero, the equation of state reduces to the ideal gas law, and the compressibility equals 1.

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DETAILS

Submission from the Compute-to-Learn course at the University of Michigan.

PERMANENT CITATION

Alicia Rae Welden

Do you see this quantity V by V minus b minus a by V RT, so what they do is that they just plot the value of Z and vary V basically, you can plot the whole right hand side quantity, you do not have to really separate it out, right. So you can put plot you can put value V as 1 and 2 and things like that and just calculate the corresponding Z value, okay.

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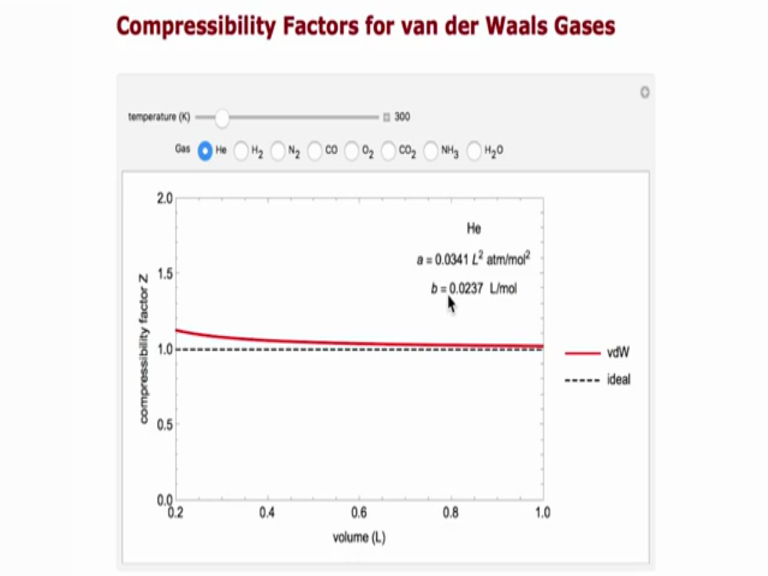

Compressibility Factors for van der Waals Gases

temperature (K) 300

Gas ● He ○ H_2 ○ N_2 ○ CO ○ O_2 ○ CO_2 ○ NH_3 ○ H_2O

He

$a = 0.0341\ L^2\ atm/mol^2$

$b = 0.0237\ L/mol$

So when you do that you get this expression which is shown in red colour, okay so what you see here is that for helium gas you see that Z value even for very low volume it is above 1 because a is small and b is also small.

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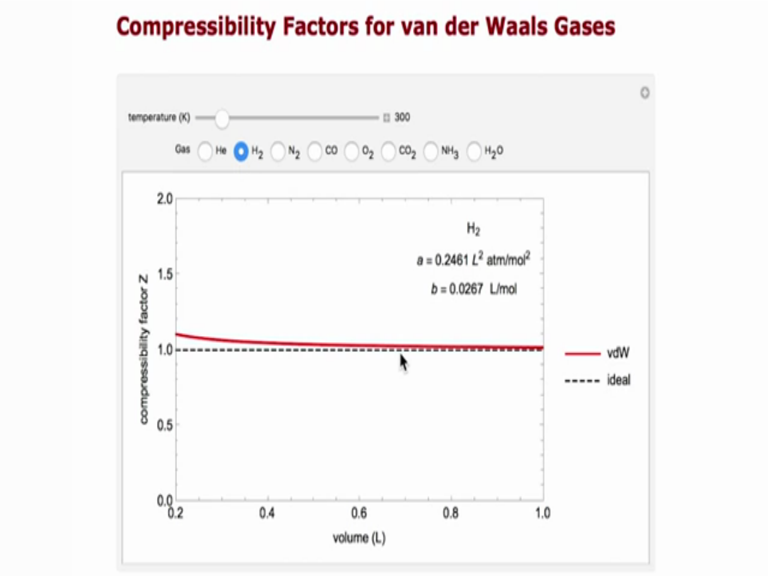

Compressibility Factors for van der Waals Gases

temperature (K) 300

Gas ○ He ● H_2 ○ N_2 ○ CO ○ O_2 ○ CO_2 ○ NH_3 ○ H_2O

H_2

$a = 0.2461\ L^2\ atm/mol^2$

$b = 0.0267\ L/mol$

Now when you go to hydrogen, so when it is helium a is 0.03, when you go to hydrogen it is 0.24 that means it significantly increases by almost 8 times.

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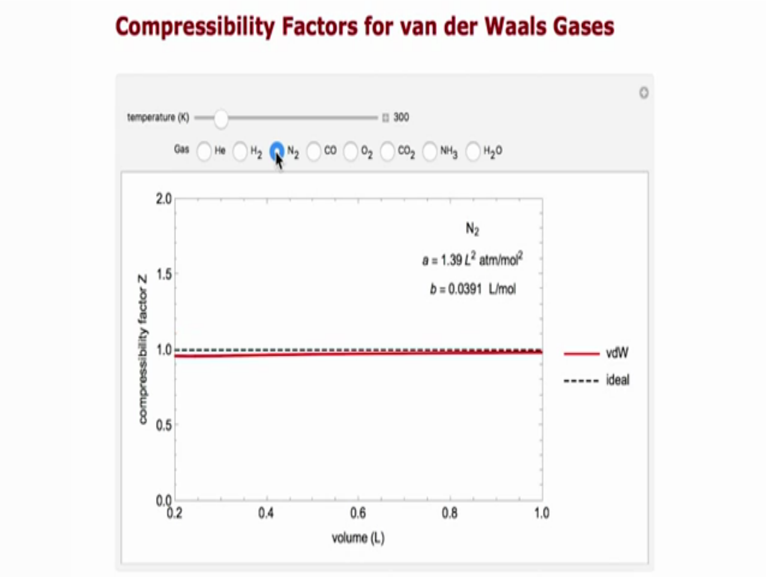

Compressibility Factors for van der Waals Gases

temperature (K) 300

Gas ○ He ○ H_2 ● N_2 ○ CO ○ O_2 ○ CO_2 ○ NH_3 ○ H_2O

When you go to nitrogen it is 1.39 a value is much more and you see it has already come below 1.

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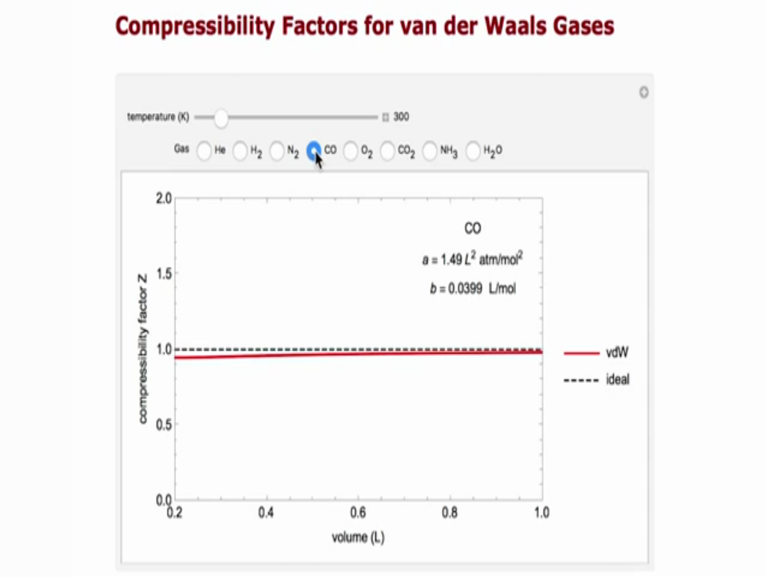

Compressibility Factors for van der Waals Gases

temperature (K) 300

Gas ○ He ○ H_2 ○ N_2 ● CO ○ O_2 ○ CO_2 ○ NH_3 ○ H_2O

Now you go to carbon monoxide it is below 1.

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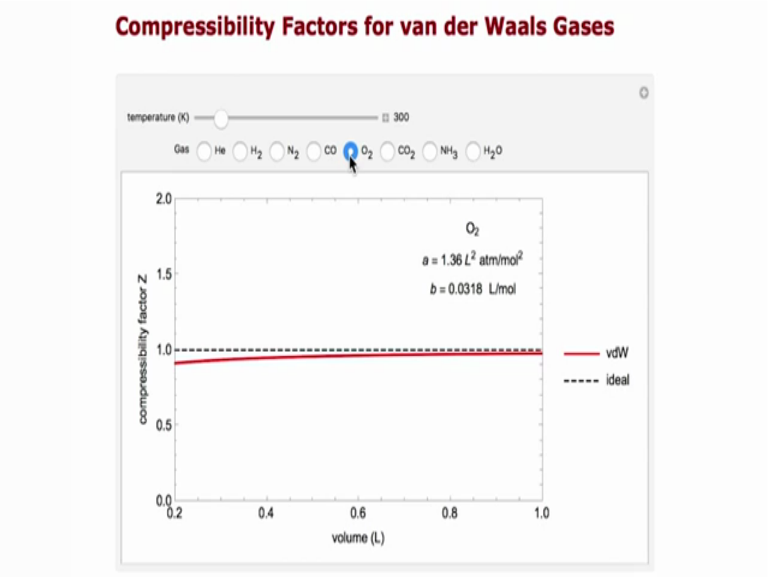

Compressibility Factors for van der Waals Gases

temperature (K) 300

Oxygen it is even below.

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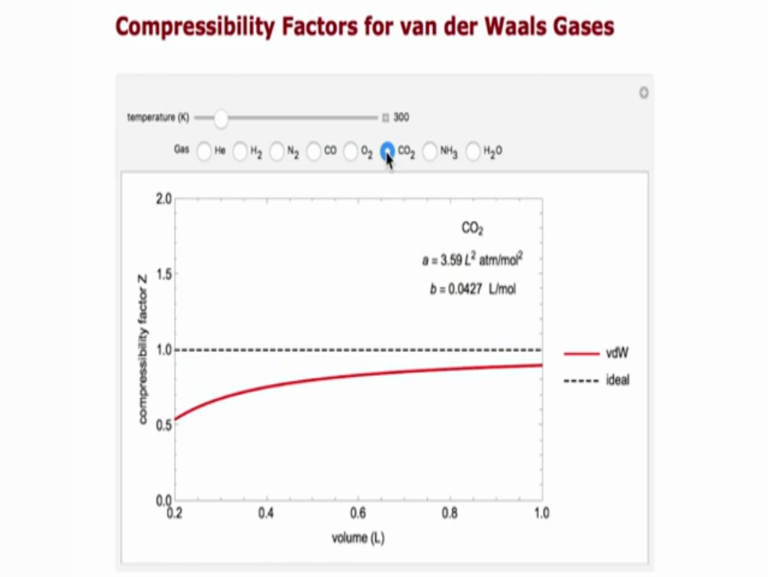

Compressibility Factors for van der Waals Gases

temperature (K) 300

Carbon dioxide.

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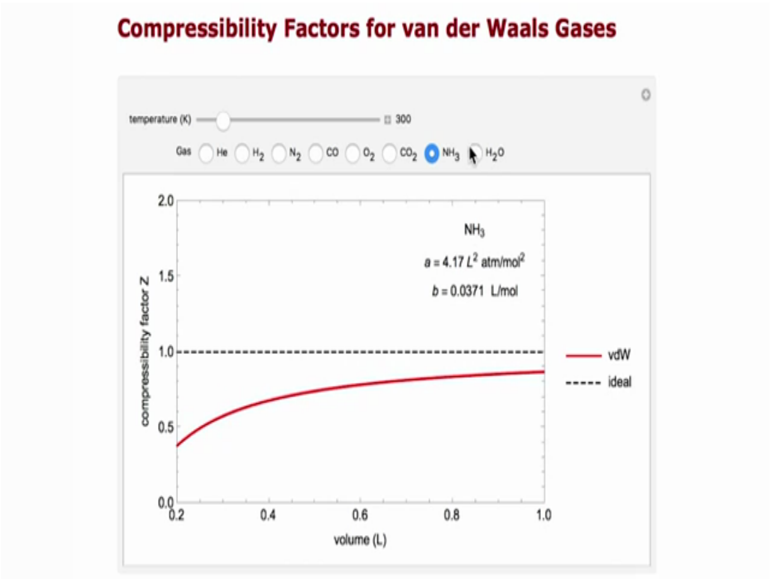

Compressibility Factors for van der Waals Gases

temperature (K) 300

Gas ○ He ○ H_2 ○ N_2 ○ CO ○ O_2 ○ CO_2 ● NH_3 ○ H_2O

NH_3

$a = 4.17\ L^2\ \text{atm/mol}^2$

$b = 0.0371\ \text{L/mol}$

And ammonia is you see how it is.

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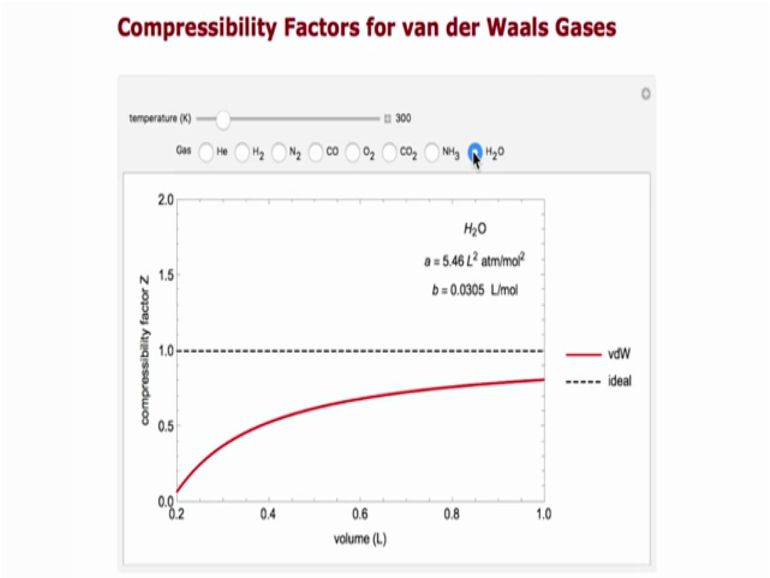


Compressibility Factors for van der Waals Gases

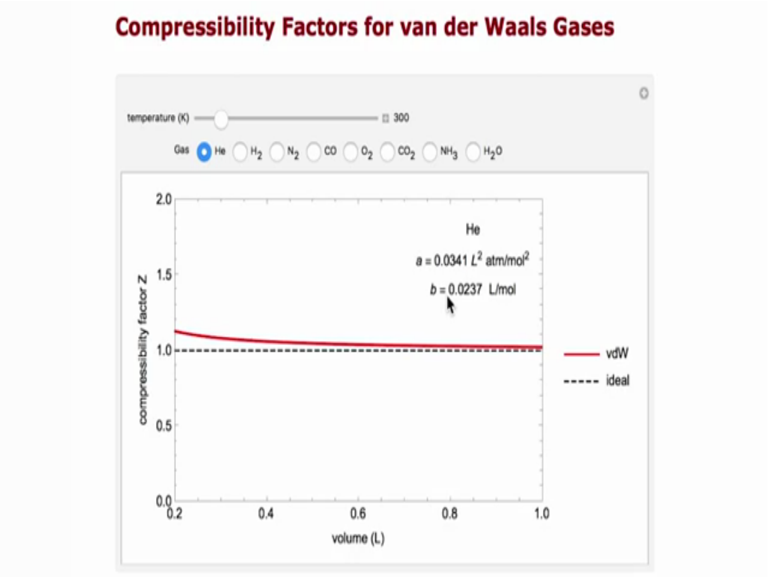
temperature (K) 300

Gas ○ He ○ H_2 ○ N_2 ○ CO ○ O_2 ○ CO_2 ○ NH_3 ● H_2O

H_2O

$a = 5.46\ L^2\ \text{atm/mol}^2$

$b = 0.0305\ \text{L/mol}$



Compressibility Factors for van der Waals Gases

temperature (K) 300

Gas ● He ○ H_2 ○ N_2 ○ CO ○ O_2 ○ CO_2 ○ NH_3 ○ H_2O

He

$a = 0.0341\ L^2\ \text{atm/mol}^2$

$b = 0.0237\ \text{L/mol}$

And then finally water which has the highest value of a and remember we told you that a indicates interaction, higher the value of a stronger the interaction is between the particles, so therefore if a increases then automatically the compressibility will be lower than 1. So as you see that because of the a it is going lower than 1 and we have seen that when it will be larger than it will go above and b also has b will not vary so much because b is just the size of the molecule, so going from helium to water is not that significant.

So for example it is going almost you know 30, 40 times between helium and the water but b value is not changing that much, it will be at most the double, right. So b value of water is 0.03 litre per mole for helium it is 0.02, so you see b value does not change that much, only the a value which is interaction that changes strongly and therefore it has that kind of effect.