Introduction to Chemical Thermodynamics and Kinetics

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Lecture – 03
Properties of Gases

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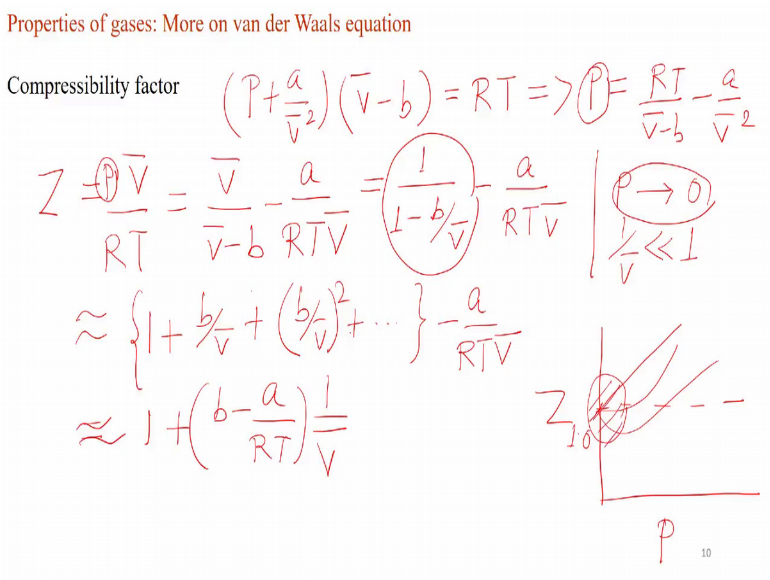

Properties of gases: More on van der Waals equation

Compressibility factor

$$\left(P+\frac{a}{\bar{V}^2}\right)(\bar{V}-b)=RT \Rightarrow \boxed{P}=\frac{RT}{\bar{V}-b}-\frac{a}{\bar{V}^2}$$

$$Z=\frac{\boxed{P}\bar{V}}{RT}=\frac{\bar{V}}{\bar{V}-b}-\frac{a}{RT\bar{V}}=\boxed{\frac{1}{1-b/\bar{V}}}-\frac{a}{RT\bar{V}} \quad \Bigg| \quad \boxed{P\to 0} \quad \frac{1}{\bar{V}}\ll 1$$

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

$$\approx 1+\left(b-\frac{a}{RT}\right)\frac{1}{\bar{V}}$$

Now, let us discuss how van der Waals gas equation can explain the nature of the compressibility factor. Now, remember the van der Waals gas equation is P plus a by V square V minus b is equal to RT which we are rewriting as P is equal to RT divided by V minus b minus a by V square. Now, the compressibility factor was defined as Z equal to PV divided by RT. Now, we will use the value of P obtained from van der Waals gas equation and insert it into the expression for compressibility factor to get which can be rewritten as; now, remember that in order to explain the compressibility factor or the behaviour of the compressibility factor in the low pressure region we can actually make an approximation.

Since, P tends to 0, in the low pressure region which means 1 over V bar is also tends to 0 and must be very much less than 1. So, we can actually express this first term in terms of at a lower expansion and write the compressibility factor as, this is the Taylor series expansion for the first term and then there is an additional term. Now, we can ignore the higher order terms because in the limit P tends to 0, 1 over V bar also tends to 0. So, we can just use the values only up to 1 over V bar, thus we get.

Now, remember how the compressibility curve looks like. It was Z versus P and then this was the ideal behaviour at Z equal to 1 and then for a definite gas the higher temperature curve look like this, the lower temperature curve look like this and the intermediate temperature curve look like this. So, we are trying to explain the behaviour at a very low pressure region or in this region. So, in order to do that we need to understand, what is the slope of the curve? We can calculate it from the expression of the compressibility factor using van der Waals gas equation, which we just obtained.

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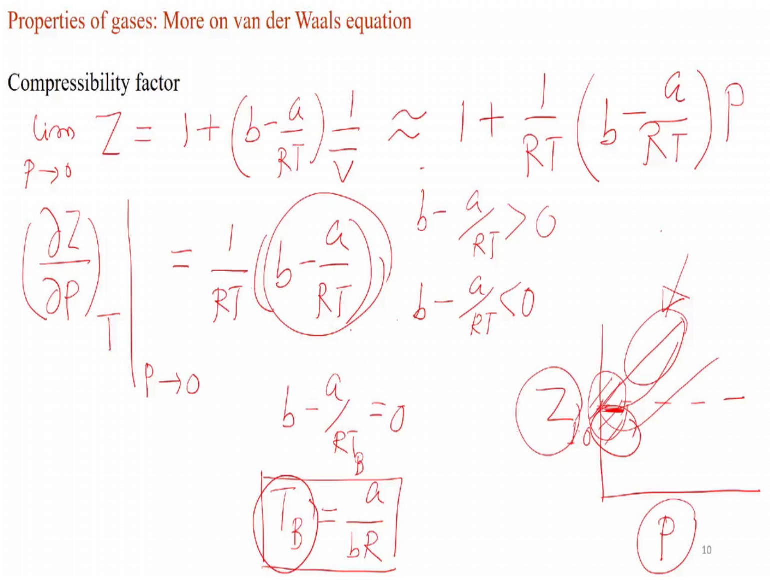

Properties of gases: More on van der Waals equation

Compressibility factor

$$\lim_{P\to 0} Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} \approx 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)P$$

$$\left(\frac{\partial Z}{\partial P}\right)_T\Bigg|_{P\to 0} = \frac{1}{RT}\left(b - \frac{a}{RT}\right)$$

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

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

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

$$\boxed{T_B = \frac{a}{bR}}$$

So, what we arrived at for the expression of compressibility factor in the limit of very low pressure is, now, remember the compressibility factor expression of the plots were Z versus P or pressure, but in this equation we have molar volume. So, what we can do instead is writing the molar volume in terms of P. Now, strictly speaking since we are using van der Waals gas equation we should use the expression of P in terms of volume. However, since we are working or we are only trying to explain the behaviour in the very low pressure region we can also use the ideal gas equation for the expression of the molar volume which will give the expression for compressibility factor as 1 plus 1 over RT b minus a by RT into P.

Now, in order to understand the slope of this curve at constant temperature in the limit when P tends to 0, we get an expression like 1 over RT into b minus a by RT. So, the important quantity here, which will dictate the nature of the slope whether it is positive slope negative slope or 0 is b minus a by RT. If b minus a by RT is greater than 0, the slope is positive which will explain this region, which explains these type of curves when b minus a by RT is less than 0 that will explain the negative slope of curves for some other temperature and when b minus a by RT is 0, that will explain when the curve flattens out near 0 pressure. We just said that this temperature is known as Boyle temperature. So, we can get an expression for the Boyle temperature which we wrote as T suffix B as a by b R.

So, the van der Waals gas equation yields an expression for the Boyle temperature in terms of the constants a and b which means these Boyle temperature will be different for different gases as a and b are constants which are different for different gases which is experimentally observed also.

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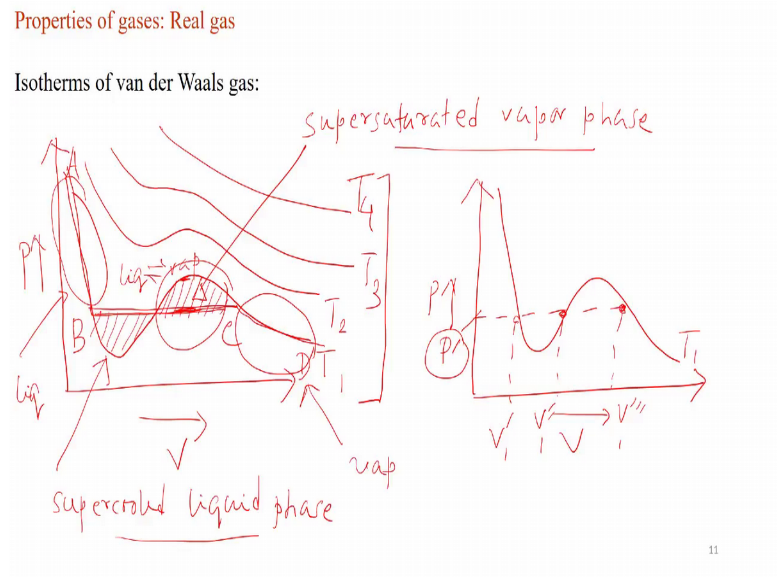

Properties of gases: Real gas

Isotherms of van der Waals gas:

Now, let us try to draw the isotherms for the van der Waals gas equation. So, I have drawn isotherms for 4 different temperatures. Now, look at the first curve which is at temperature T 1; here, notice carefully that if you recall the curve which was obtained by Andrews which were for real gas that had a nature like this curve A, B, C, D, which we discussed. Now, if you compare the Andrews curve with the curve that we obtained from the model which is van der Waals gas equation, we get striking similarity in the region CD and AB which explain the region where the substance is present as vapour or the region where the substance is present in liquid. However, in the region when the substance is present as equilibrium between liquid and vapour.

The van der Waals gas equation gives a very different result from what is observed experimentally. We see that there is a rise region or high region and there is a deep region. So, this kind of peak and trough behaviour is not observed experimentally. So, if you carefully watch here this region, here, the pressure is actually higher than what it would be for the vapour pressure. So, this region is termed as super saturated vapour phase. Similarly, the deep region or the trough region is called the super cooled liquid phase. These 2 phases are not real phases and they are metastable phases which we caught by plotting the van der Waals gas equation. Remember, the reality is the experimental curve which was obtained by Andrews.

Now, we have a very interesting situation for the van der Waals curve. Let us redraw the curve at T 1 let us also draw a line which is parallel to the volume axis. Now, as you can see that at this pressure which we can term as P prime there exists 3 different volumes which we can denote as V prime 1, V double prime 1, V triple prime 1 which all corresponds to the temperature T 1.

Now, what does that mean? The substance can have 3 different volumes for this particular pressure. This is not surprising. This arises due to the cubic nature of the van der Waals gas equation which we are going to explore in short before that as we discussed the surface plot or the P, V, T plot for the ideal gas equation.

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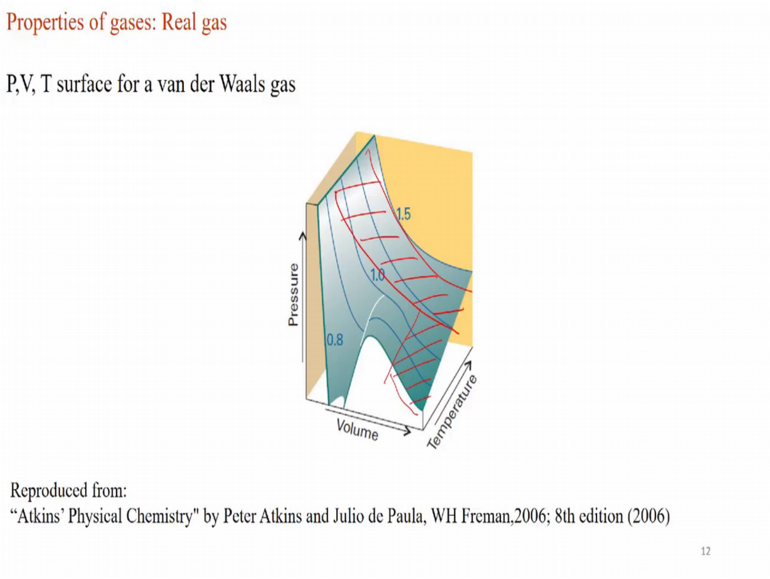

Properties of gases: Real gas

P,V, T surface for a van der Waals gas

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We can also plot similar surface plot for van der Waals gas equation as shown in this figure. As you can see at the very high temperature region, this region, the surface more or less looks like an ideal gas surface. This is not surprising because ideal gas behaviour is observed at high temperature limit. Similarly, in the very low pressure region also the surface looks like very much ideal like. So, the van der Waals gas equation can satisfactorily explain the limiting gases, that is, at high temperature and at very low pressure. The equation of state will reduce to the ideal gas equation of state or the P, V, T surface will also look like that of an ideal gas.

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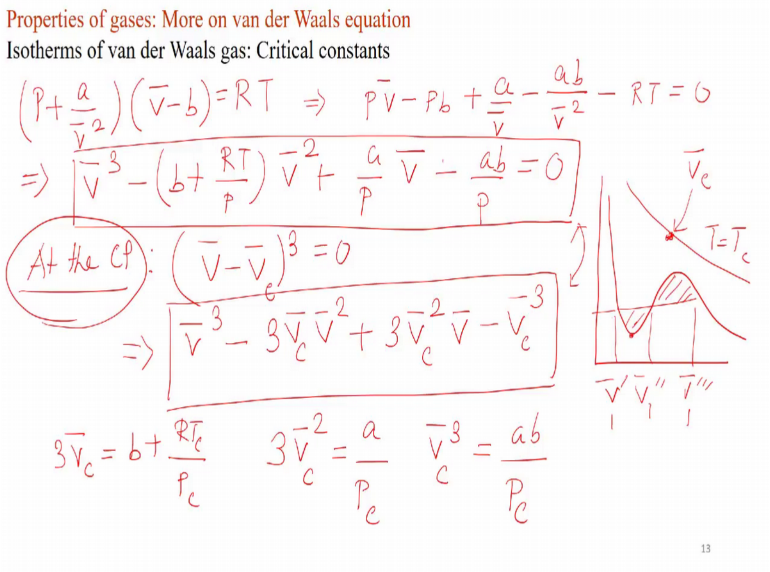

Properties of gases: More on van der Waals equation

Isotherms of van der Waals gas: Critical constants

$$\left(P+\frac{a}{\bar{V}^2}\right)\left(\bar{V}-b\right)=RT \Rightarrow P\bar{V}-Pb+\frac{a}{\bar{V}}-\frac{ab}{\bar{V}^2}-RT=0$$

$$\Rightarrow \boxed{\bar{V}^3-\left(b+\frac{RT}{P}\right)\bar{V}^2+\frac{a}{P}\bar{V}-\frac{ab}{P}=0}$$

At the CP: $\left(\bar{V}-\bar{V}_c\right)^3=0$

$$\Rightarrow \boxed{\bar{V}^3-3\bar{V}_c\bar{V}^2+3\bar{V}_c^2\bar{V}-\bar{V}_c^3}$$

$$3\bar{V}_c=b+\frac{RT_c}{P_c} \qquad 3\bar{V}_c^2=\frac{a}{P_c} \qquad \bar{V}_c^3=\frac{ab}{P_c}$$

Now, let us discuss more on the van der Waals curve or van der Waals isotherms. Now, we can expand the van der Waals gas equation as this and then we can multiply both side by molar volume square and divide by pressure to get. Now, you see that the van der Waals equation of state is actually cubic in molar volume and that was the reason why we got 3 different followings for a particular pressure.

Now, interestingly if you remember that at low temperature the curve look like this, but at critical temperature when T is equal to T c, the curve looks like this; which means all this crest and trough region they equals and all these 3 different volumes which we got for the same pressure they are equals to a single volume which we call as critical volume. So, at the critical point we can write that the roots of the equation are degenerate or the all 3 roots of the equation are degenerated. If we call that root as V c which is the critical volume, we can write. We can expand this expansion as; now, we have a very interesting situation we said that at the critical point I have an expression for a cubic equation like this and also we arrived from the van der Waals gas equation or the expansion of the van der Waals gas equation that the nature of the equation is cubic.

Now, we can compare term by term for these 2 equations to get very interesting relations. If we compare the second term with a second term or the coefficients of the second terms we get 3 V c is b plus RT c by P c, 3 V c square is a by P c and V c cube is a b by P c. The suffix c for P and T denote that we are considering the system at the critical point. So, we can now figure out very easily what are the values of a, b and c from these equations.

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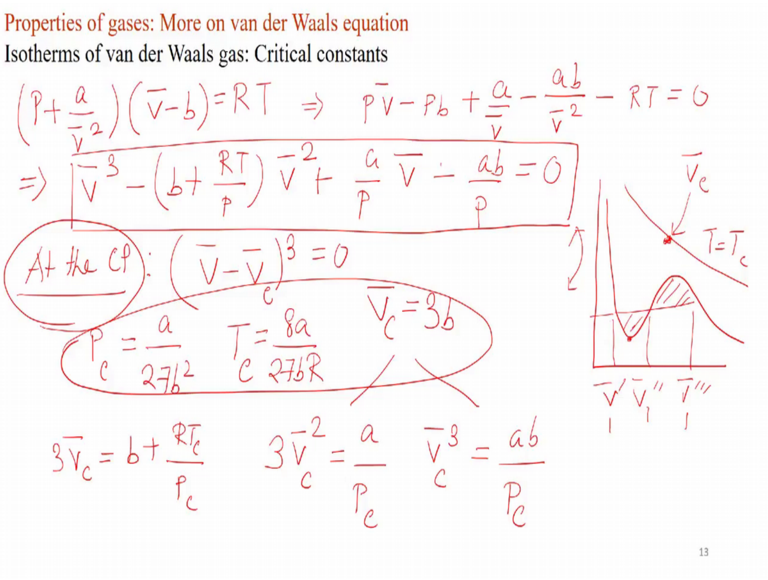

Properties of gases: More on van der Waals equation

Isotherms of van der Waals gas: Critical constants

$$\left(P+\frac{a}{\bar{V}^2}\right)(\bar{V}-b)=RT \Rightarrow P\bar{V}-Pb+\frac{a}{\bar{V}}-\frac{ab}{\bar{V}^2}-RT=0$$

$$\Rightarrow \boxed{\bar{V}^3-\left(b+\frac{RT}{P}\right)\bar{V}^2+\frac{a}{P}\bar{V}-\frac{ab}{P}=0}$$

At the CP: $(\bar{V}-\bar{V}_c)^3=0$

$$P_c=\frac{a}{27b^2} \quad T_c=\frac{8a}{27bR} \quad \bar{V}_c=3b$$

$$3\bar{V}_c=b+\frac{RT_c}{P_c} \quad 3\bar{V}_c^2=\frac{a}{P_c} \quad \bar{V}_c^3=\frac{ab}{P_c}$$

For example; if you take these 2 equations and divide the second equation by the first equation you will get a equation in terms of V c and then the value of V c will be given by just V c equal to 3 b. Similarly, you can get the values of P c as a by 27 b square and also the value of T c as 8a by 27 b R. So, these are the values of the critical constants which are P c, T c and V c in terms of the van der Waals gas constants a and b.

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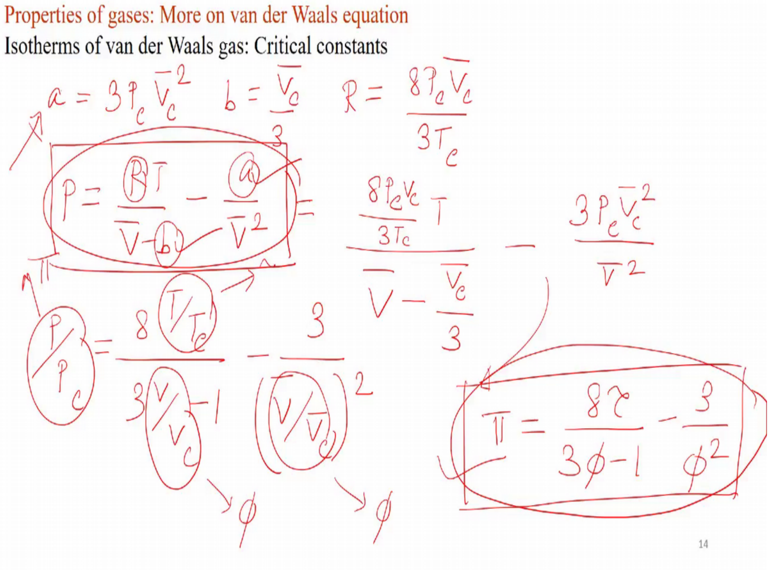

Properties of gases: More on van der Waals equation

Isotherms of van der Waals gas: Critical constants

$$a=3P_c\bar{V}_c^2 \quad b=\frac{\bar{V}_c}{3} \quad R=\frac{8P_c\bar{V}_c}{3T_c}$$

$$\boxed{P=\frac{RT}{\bar{V}-b}-\frac{a}{\bar{V}^2}}=\frac{\frac{8P_c\bar{V}_c}{3T_c}T}{\bar{V}-\frac{\bar{V}_c}{3}}-\frac{3P_c\bar{V}_c^2}{\bar{V}^2}$$

$$\underbrace{P/P_c}_{\Pi}=\frac{8\,\overbrace{(T/T_c)}^{\tau}}{3\underbrace{(\bar{V}/\bar{V}_c)}_{\phi}-1}-\frac{3}{\underbrace{(\bar{V}/\bar{V}_c)}_{\phi}^{2}}$$

$$\boxed{\Pi=\frac{8\tau}{3\phi-1}-\frac{3}{\phi^2}}$$

Now, we could alternatively do another thing. We could write a and b and also the molar gas constant R in terms of the critical constant. If we just rearrange the expression for V c, P c and T c which we just obtained we will get a is 3 P c the V c square, b is V c by 3 and R is 8P c V c by 3 T c.

Now, let us do one thing; let us incorporate these values of a, b and R into the original van der Waals gas equation which is P is equal to remember, it was a by V square and if we now incorporate the values of R, a and b from this expression which we just derived we get a very interesting relationship. This is the expression for RT divided by V minus b, expression for b is V c by 3 and then a by V square expression for a is 3 P c V c square divided by V bar square.

Now, we can rearrange this nicely to get P by P c is equal to 8 into T by T c divided by 3 into V by V c minus 1, minus 3 into V by V c squared. This is just rearranging this equation. Now, we have a very beautiful situation. What is P by P c? It is the ratio of the pressure to the critical pressure. Similarly, T by T c is a ratio of the temperature to the critical temperature and V by V c is the ratio of a molar volume to the critical molar volume.

Now, if we denote these quantities by pi, tau and phi respectively. We can write the van der Waals gas equation in a very compact form which reads as pi is equal to 8 tau divided by 3 phi minus 1, minus 3 divided by phi square. So, this is known as the reduced form of the van der Waals equation, because pi equal to P by P c is known as the reduced pressure, V equal to V by V c is known as the reduced volume and similarly, tau equal to T by T c is known as the reduced temperature.

Now, why we did it or what is the point of arriving at this reduced expression. Of course, it is a compact expression, that is, point number one. But, most importantly it teaches us something else look at the original van der Waals gas equation which is this equation contains constants like a and b which are specific for a particular gas molecule. However, the reduced expression does not have any particular constant that represents one particular gas, which means just like in an ideal gas there was no particular constant which is specific to a gas. We have reduced the van der Waals equation also in a similar form which is independent of a constant which is very specific to a particular gas.

So, the loss of generality which was there in this original van der Waals gas equation has been regained in the van der Waals equation when it is written in the reduced form which means that if we do an experiment and plot say the compressibility factor as a function of not the pressure, but the reduced pressure using this reduced equation of state. We should get similar curve for all the gases.

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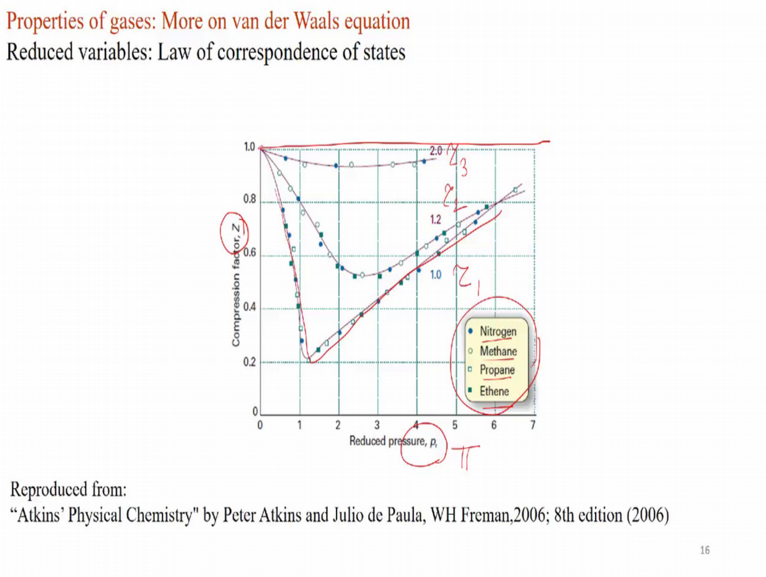

Properties of gases: More on van der Waals equation

Reduced variables: Law of correspondence of states

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To convince you this fact, here, I show you the expression or the plots for compressibility factor as a function of reduced pressure, which we will denote it as pi. Now, note that this is plotted at various tau values or the reduced temperature. For a given tau, all the gases like nitrogen, methane, propane and ethane, they behave very similar. They all fall on the same curve, for any given temperature which means they all now behave similarly. But, now the trick is that they are not behaving ideal because if they had behaved ideally the value will be just the curve will look like just a flat line and Z equal to 1 which is the ideal behaviour.

So, what we did is that we cleverly replaced the constants a and b by the critical constants which are T c, P c and V c and by taking the ratio of the pressure to the critical pressure and so on, we have defined few parameters which are reduced parameters and if we plot the compressibility factor against the reduced pressure it is no surprising that all the gas molecules should behave similar way, because there is no explicit constant in the equation that explains a particular or that actually corresponds to a particular gas molecule.

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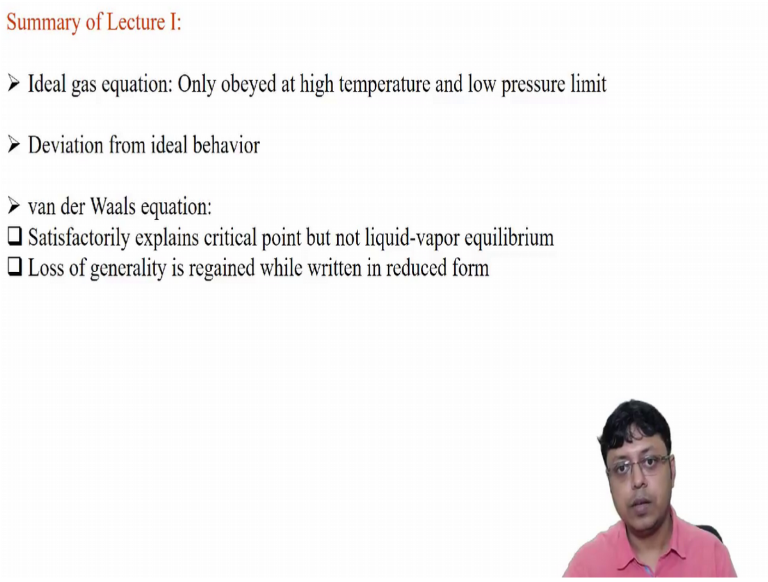

Summary of Lecture I:

- ➢ Ideal gas equation: Only obeyed at high temperature and low pressure limit
- ➢ Deviation from ideal behavior
- ➢ van der Waals equation:

☐ Satisfactorily explains critical point but not liquid-vapor equilibrium
☐ Loss of generality is regained while written in reduced form

So, let me summarise what we discussed so far. We started with a discussion of ideal gas equation. We showed that ideal gas equation is only a hypothetical situation; however, real gases can obey the ideal gas situation only in limiting gases, when the temperature is too high or the pressure is too low. Secondly, we discussed the deviation from the ideal behaviour; there we discussed 2 main experiments the variation of the compressibility factor with pressure as well as the isotherms for the real gases which are known as Amagat's curve and Andrews curve respectively.

Then, we discussed the development of a model which is the van der Waals model and we discussed in details the van der Waals gas equation. We discussed how van der Waals gas equation satisfactorily explains the existence of a critical point, but it cannot explain the liquid vapour equilibrium region. We also wrote the van der Waals gas equation in a very compact form and said the loss of generality which was in the original form of the van der Waals equation where a and b constants were included, that loss generality is regained in it is reduced form which is more compact to use.

In the next lecture, we will start our discussion on classical thermodynamics. We will first define few terms and then we will move on and see how we can calculate different quantities which are measurable quantities for ideal gas as well as for a real gas and for the real gas we will use the model of van der Waals equation.

Now, before we finish there are also many other models that are more accurate than the van der Waals model, however, we will frequently use the van der Waals model here, because of its simplicity of use.

Thank you.