Chemical Engineering Thermodynamics
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Lecture - 15
Thermodynamic Property Calculation using Cubic EoS

Hello and welcome back. Today we are going to look at Cubic Equations of State and if you recall our goal was to be able to do changes in property or the changes in various thermodynamic properties involving equation of state. We involve equation of state because not all fluids behave as an ideal gas.

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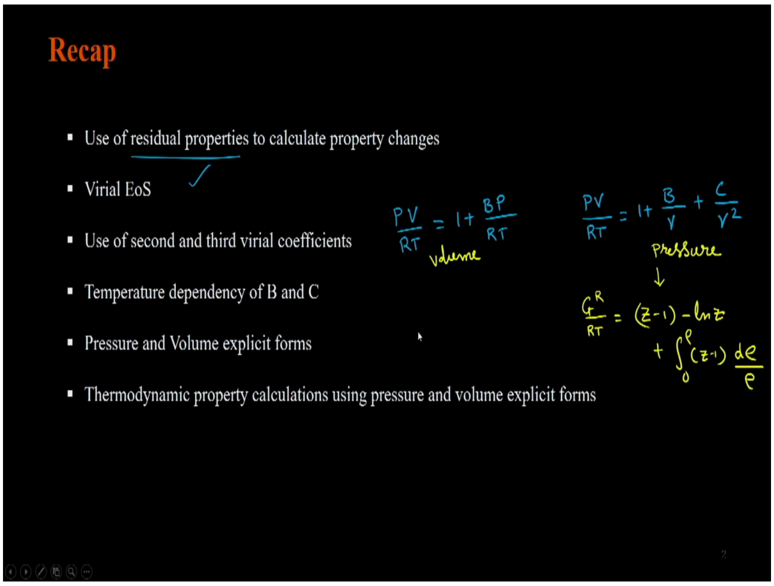

Recap

- Use of residual properties to calculate property changes ✓
- Virial EoS
- Use of second and third virial coefficients
- Temperature dependency of B and C
- Pressure and Volume explicit forms
- Thermodynamic property calculations using pressure and volume explicit forms

$\frac{PV}{RT} = 1 + \frac{BP}{RT}$ volume

$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2}$ pressure

$\downarrow$

$\frac{G^R}{RT} = (Z-1) - \ln Z + \int_0^{\rho} (Z-1) \frac{d\rho}{\rho}$

And if we have non-ideal gases then we introduced the concept of residual properties that would allow us to account for that non-ideality. One of the ways we have looked at is using virial equation of state involving both the second and the third virial coefficients. If we only have the second virial coefficient we have written equation of state as P V over R T is 1 plus B P by R T. And, if we want to involve both the second and the third virial coefficients then we write it in a pressure explicit form such as 1 plus B by V plus C by V square.

So, one of them is explicit in volume and the other one is explicit in pressure. And, depending on which form we use it is convenient to express the residual properties in different ways. For example, if I have the pressure explicit form of equation of state such as this one then recall that we have written G R over R T that residual Gibbs free energy as z minus 1 minus l n z plus integral of 0 to rho z minus 1 d rho over rho. We can take this as our generating function and generate all the other residual properties based on this expression.

Similarly we had another form of an equivalent expression for volume explicit equation of state if there is only the second virial coefficient. Now, the virial equation of state are suitable only in particular ranges of the fluid particular temperature and pressure ranges for the fluid and it is suitable only for the gas phase. The other equation of state that is commonly used is what is known as a cubic equation of state.

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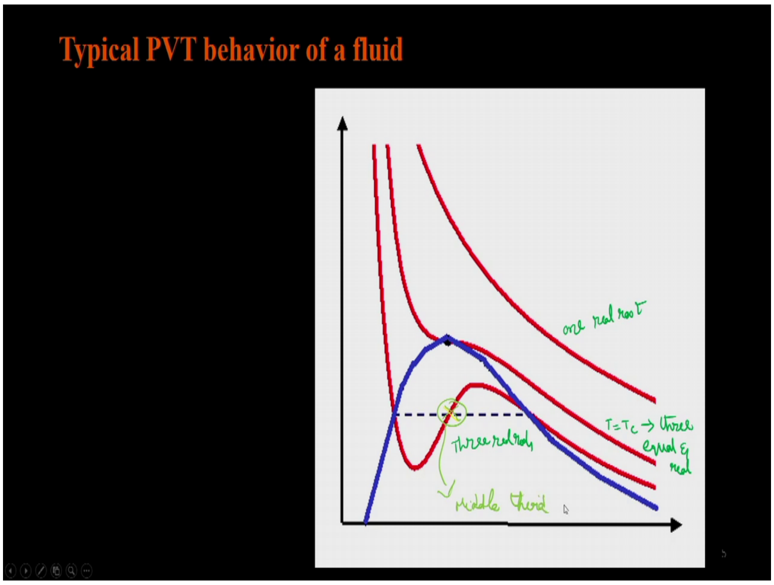

Typical PVT behavior of a fluid

To understand and appreciate this cubic equation of state, let us start looking at a typical PVT behavior of a fluid alright. Let us quickly go back and summarize the typical PVT behavior of a fluid. As you can see I have a typical PVT behavior of a fluid in this particular figure. On the x axis I have the molar volume V and on the y axis I have the pressure P and the red curves are isotherms drawn at different temperatures. The blue curve is the vapour dome as it is called or it represents the two phase region, if you recall our discussion from the thermodynamic diagrams.

There are certain regions in this curve where the temperature is greater than the critical temperature then the fluid is going to exist only in a single phase. At temperatures below the critical temperature the fluid there are certain portions of the curve where, the fluid will exist only as a liquid or only in the vapor phase. And in between or underneath the dome whenever we fall underneath the dome then the fluid will exist in the two phases. When we say it exists in two phases there is going to be a mixture of liquid and vapour that will be in equilibrium at that particular condition.

Now, let us consider a scenario when the temperature is below the critical temperature. Let us take an example of a piston and a cylinder assembly and let us say I have only the liquid phase region. I start of at this point J which corresponds to this I am only in the liquid phase region. As I withdraw this piston up I am lowering the pressure, I am increasing the volume. I will reach a state where I will hit this point K. And at this point K I hit the vapour dome or the first bubble of vapor forms most of it is still liquid, but there is just that one bubble of vapor that is formed when I hit this dome.

Now, if I withdraw this piston more then obviously, I am increasing the total volume of the system. But, once I hit the vapor dome the system is going to be at a constant pressure and constant temperature until it reaches this liquid, the saturated liquid condition. So, this point K corresponds to saturated vapor and this point L corresponds to saturated liquid. And I withdraw the piston after K there will be a vapor and a liquid phase that coexist. And, as I keep withdrawing this the amount of vapor phase inside the piston cylinder assembly is going to increase and the amount of liquid inside it will decrease. Until it reaches this point L where, most of it is going to be vapor except that one drop of liquid; except that one drop of liquid everything is going to be in the vapor phase right. So, that is the other extreme.

So, between this K and L even though I am withdrawing the piston all that happens is that the relative amounts of the vapor and the liquid in inside the assembly; piston cylinder assembly are going to change. After this point L, if I withdraw the piston even more than it will be only completely vapor and, then I go to the right of the dome and that would be only again a single phase in this case a single vapor phase right.

So, this is how a typical fluid behaves when it passes through a two phase region. As you can see the densities or the molar volumes of the vapor and the liquid phases and K and L are widely different. If I increase the temperature and go through this point, let us draw it in a different colour, go through this point well I can see that can I; let us use that guy right.

I can increase that, I will go through this and as you can see the difference in the densities of the liquid and the vapor phases are much closer to one another than they were when the temperature was lower at the red curve here right. This difference between the liquid and the vapor densities are of the on the red curve are much further away than they are for the purple curve.

I can keep increasing the temperature until I reach such a condition where the temperature where the difference between the vapor and liquid densities is almost negligible. They are they are exactly identical and at that particular temperature where the liquid and vapor densities passing through the two phase region are going to be identical is going to be equal to what we call as the critical temperature.

That condition where both the densities of the liquid and vapor are going to be equal is called as the critical point. Above critical point of course, I will only have the single phase, I cannot make a liquid in this region. The other interesting thing to note in this isotherm is that within the liquid phase region right within this region here, when I am in the liquid phase region the isotherm is very very steep indicating that the change in pressure is not going to change volume as much as it did in case of a liquid.

Now, in case of a vapor now in case of a vapor if I change the pressure right; if I change the pressure if I increase the pressure the volume is changing significantly here. But, here even if I change the pressure by quite a bit the change in volume is pretty small. So, the isotherm is very steep; this is indicative of the fact that liquids are fairly incompressible right.

So, the change in volume is going to be pretty small compared to change in pressure. This region where T is greater than T c in reality is actually the gas phase region. And, the region where T is below T c is the vapor phase region although we use these two terms synonymously; vapor usually corresponds to the temperatures below the critical temperature. Temperatures above critical temperature are known as the gas phase regions and if both T and P are greater than T c and P c then we call that as a supercritical region. So, this is a typical three PVT behavior of a fluid. And, a cubic equation of state actually captures most of this behavior as you can see for temperatures below the critical temperature; if I take any pressure there are 3 volumes for any given temperature and pressure right V 1 V 2 and V 3 for this particular point.

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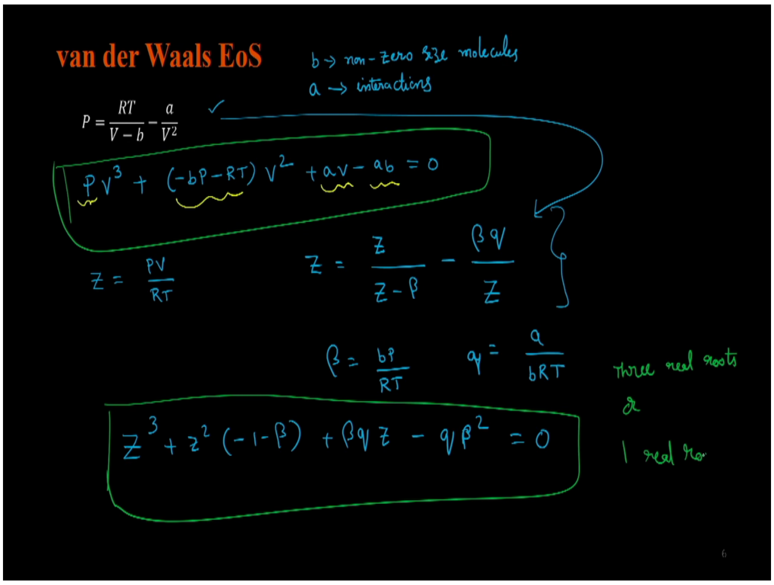

van der Waals EoS

b → non-zero size molecules

a → interactions

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

$$\boxed{PV^3 + (-bP-RT)V^2 + aV - ab = 0}$$

$$Z = \frac{PV}{RT}$$

$$Z = \frac{Z}{Z-\beta} - \frac{\beta q}{Z}$$

$$\beta = \frac{bP}{RT} \qquad q = \frac{a}{bRT}$$

$$\boxed{Z^3 + z^2(-1-\beta) + \beta q z - q\beta^2 = 0}$$

three real roots

or

1 real ro

So, this is well represented by what is known as a cubic equation of state. So, we are talking about a cubic polynomial which is cubic in volume that represents the PVT behavior. One of the famous cubic equations of state early on is given by van der Waals; its expression as most of you are familiar with is P equals RT by V minus b minus a by V square. So, this b term corresponds to the original development of the van der Waals equation goes as such, the V term corresponds to the non-zero size of the molecules right.

They have a finite size and a term is to account for interactions among the molecules. The ideal gas assumes that there are no interactions and all molecules are do not have any size which of course, is not true. So, a term accounts for those interactions, well the b term accounts for the finite size of the molecules. And, this is the expression given by van der Waals for PVT behavior of such fluid. And as you can see this expression is cubic in volume right. If I actually expanded and write it as a cubic then this equation you can easily rewrite this equation reads like this, minus b P minus R T times V squared plus a V minus a b equal to 0.

So, these are the coefficients for the cubic equation in terms of volume right this, this, this and this usually these cubic equations of state are much better handled with the compressibility factor z as you can recall z is P V over R T. So, I can rewrite this whole expression in terms of z and it would read z is z over z minus b beta minus beta times q over z right where, beta is actually related to b as b P over R T and q is and q is related to both a and b as q is a by b RT. So, once we make these two substitutions and rewrite the van der Waals equation of state it will give us an equation which reads as such.

And in this is of course, a cubic in the compressibility factor z as well plus z squared minus 1 minus beta plus beta times q times z minus q times beta squared is 0. This is the cubic in volume we and cubic in the compressibility factor z. So, depending on the convenience we can use one of the two equations right. So, when we solve these equations we get either three real roots or 1 real root.

Now, if you look at this there are certain regions in the curve where we have three real roots, there are certain regions in the curve where we have one real root alone. And in this region there will be three real roots right and in fact, at T equal to T c we have three equal and real roots. So, depending on the coefficients we will end up in either a region where, we have only one real root or a region where all the three roots are equal or a region where we have three real unequal roads and, van der Waals equation can pretty much capture that type of a behavior.

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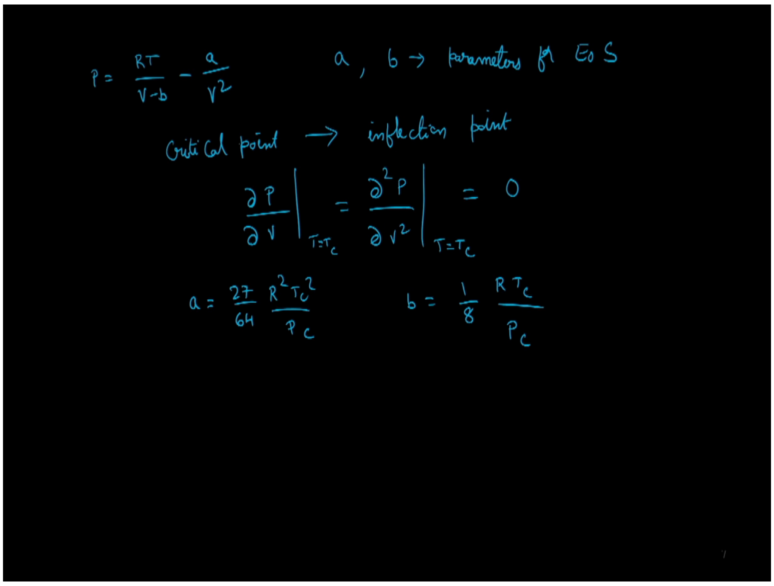

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

a, b → parameters for EoS

Critical point → inflection point

$$\left.\frac{\partial P}{\partial V}\right|_{T=T_c} = \left.\frac{\partial^2 P}{\partial V^2}\right|_{T=T_c} = 0$$

$$a = \frac{27}{64}\frac{R^2 T_c^2}{P_c} \qquad b = \frac{1}{8}\frac{R T_c}{P_c}$$

Now, the next thing we want to talk about are the two constants in the van der Waals equation of state; if you look at the two constants P is R T by V minus b minus a by V squared. Now, if you look at these two constants right these two constants a and our parameters as they are called. This is parameters for van der Waals equation of state, used the way usually we get them is by taking the critical point; mathematically it corresponds to the inflection point in the isotherm right.

So, by inflection point we mean the first and the second derivatives. The first and the second derivatives are going to be at constant temperature with respect to volume derivatives of pressure with respect to volume are going to be 0 which means we can, this occurs at the critical point of course. And, we can use the equation of state with these two criteria to get corresponding expressions for a and b. It turns out that a would be 27 over 64 R squared T c squared over P c. And, b is 1 over 8 R T c over P c. This is how we usually get the constants for or the parameters for an equation of state.

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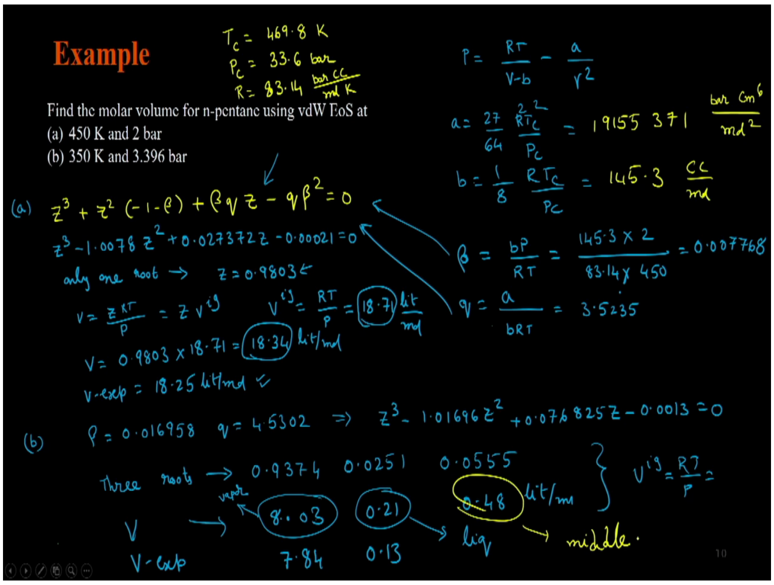

Example

$T_c = 469.8$ K
$P_c = 33.6$ bar
$R = 83.14 \frac{\text{bar cc}}{\text{mol K}}$

Find the molar volume for n-pentane using vdW EoS at
(a) 450 K and 2 bar
(b) 350 K and 3.396 bar

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

$$a = \frac{27}{64}\frac{R^2T_c^2}{P_c} = 19155371 \ \frac{\text{bar cm}^6}{\text{mol}^2}$$

$$b = \frac{1}{8}\frac{RT_c}{P_c} = 145.3 \ \frac{\text{cc}}{\text{mol}}$$

(a) $z^3 + z^2(-1-\beta) + \beta q z - q\beta^2 = 0$

$z^3 - 1.0078 z^2 + 0.027372 z - 0.00021 = 0$

$$\beta = \frac{bP}{RT} = \frac{145.3 \times 2}{83.14 \times 450} = 0.007768$$

$$q = \frac{a}{bRT} = 3.5235$$

only one root → $z = 0.9803$

$V = \frac{zRT}{P} = zV^{ig}$ $\quad V^{ig} = \frac{RT}{P} = \boxed{18.71} \ \frac{\text{lit}}{\text{mol}}$

$V = 0.9803 \times 18.71 = \boxed{18.34}$ lit/mol

V-exp = 18.25 lit/mol ✓

(b) $\beta = 0.016958 \quad q = 4.5302 \Rightarrow z^3 - 1.01696 z^2 + 0.076825 z - 0.0013 = 0$

Three roots → 0.9374 0.0251 0.0555 $\Big\} \ V^{ig} = \frac{RT}{P} =$

$V \longrightarrow \boxed{8.03}$ $\quad \boxed{0.21}$ $\quad \boxed{0.48}$ lit/mol

V-exp 7.84 0.13

Let us try to then use these ideas for van der Waals equation of state and solve one quick example. We want to find the molar volume for n pentane using van der Waals equation of state at 450 Kelvin and 2 bar and then at 350 Kelvin and 3.396 bar. So, to be able to do that if you recall the equation of state involves two parameters a and b which we want to calculate first 27 by 64 R T c over P c and b is 1 over 8 R T c R square T square by P c and R T c by P c. When I calculate these two parameters and to be able to do that what we need, then are the corresponding critical constants or the corresponding critical constants.

So, I used a handbook and taking these two critical constants from the handbook. The critical pressure is 33.6 bar and the critical temperature for pentane happens to be 469.8

Kelvin from my reference. So, if I use these two values along with the appropriate value for R so, my units are going to be as such. So, I am going to use a value of R in bar c c per mole per Kelvin so, it is 83.4 bar c c per mole Kelvin. So, if I use these units my molar volume is going to be in c c per mole; you can make appropriate conversions as then need be. For now, let us use these units and the value I have for a using these units is 19155 371 and 145.3; these are the values I get using T c and P c for n pentane. So, this will be in c c per mole and this will be in units of bar and then centimetre to the power 6 over mole square.

So, once I have these two numbers, I can now actually go back and use the equation of state. What I will do is I will try to use the compressibility factor form, I had earlier I am going to use this form z cube plus z square into negative 1 negative beta beta q z minus q beta square equal to 0. I will try to use that form to solve for the compressibility factor z first and then we will try to get the molar volume. So, if I want to do that I first need to calculate beta and q; let me write that expression in z first z cube z squared negative 1 negative beta plus beta q z minus q beta square equal to 0. Now, I want to use this equation which means I want to calculate q and beta.

Now, remember beta is b P over R T so it depends on the actual condition, temperature and pressure conditions. So, it is going to be 145.3 times P is 2 bar over 83.14 and the temperature is 450 Kelvin. And, this works out to be 0.007768 and the q is a by b R T right. So, that would be 3.5235 according to my calculations. So, once we have q and beta I can put the expression here for both q and beta. And, rewrite this cubic equation then becomes z cube minus 1.0078 z squared plus 0.027372 z minus 0.00021 equal to 0.

Now, if I solve this cubic you can use any convenient software I have used MATLAB, but you can use any convenient software to get the roots of this polynomial. It turns out you get only one real root and that root happens to be 0.9803. This is the compressibility factor recall that the compressibility factor for an ideal gas is 1. So, this compressibility factor essentially means that we were pretty close to adjust to percent off from the ideal gas behavior. If you actually want to calculate the volume it will be z R T over P remember R T over P is the volume for the ideal gas.

So, it is actually z times V ig V ig itself is the molar volume of an ideal gas under the same conditions, but I have for V ig is 18.71 litres per mole. And, because of the value of z to be 0.98 what you get for V is 0.9803 multiplied with 18.71. So, that is 18.34 litres per mole. It turns out that the experimental value is a little away from what is predicted by van der Waals equation of state the experimental value is 18.25 litres per mole. So obviously, this correction after van using van der Waals equation of state is a much better value than what we would have had if you use an ideal gas law.

So, this is much closer to reality. This is part a for part b I can do a similar exercise. The values of a and b are not going to change, the value of beta is going to change because pressure and temperature are changing. So, the value I have for beta for part b is this much and q what I calculate is 5302. Now, if I put these values of beta and q in this equation right here, then the cubic equation I get for these conditions in z is going to be 1.01696 z squared plus 0.076825 z minus 0.0013 is equals 0. And, again turns out if I use the software to get these and get to the solution turns out I have three roots in z 9374 0.0251 and 0.0555.

And, corresponding to these three roots remember molar volume is R T over P. For this case, the molar volume we can calculate and once we calculate the molar volume you have the final volumes as z R T by P. So, this one I have this value to be I have it to be 8.03 and 0.21 litres per mole; well last one is 0.21 and this one is 0.48 litres per mole. Turns out that the experimental values corresponding experimental values are 7.84 and 0.13. This is from the experiments.

So, the van der Waals equation of state again predicts three real roots and this is in a two phase region. So, we get the three real roots and the lowest root or the smallest root corresponds to the liquid volume and the largest root corresponds to the vapor volume. And, you can see they are pretty close to what is predicted by experiment the van der Waals equation of state creates a much better experimental value with respect to the vapor root than with respect to the liquid root. And, we have an additional third root which is in the middle of the two liquid and the vapor roots. And, this rule does not have any physical significance as you have seen earlier it corresponds to metastable state right.

As you have seen here this is the third root we get when we have the cubic that yields us three roots, this is the third root. And, this third root is a metastable state which is very difficult to realize in experiments, but it is of no practical significance. So, were only interested in the two roots that are extreme one the largest root which corresponds to the vapor volume, the smallest root that corresponds to the liquid volume right. So, this is how you can use van der Waals equation of state to predict the PVT behavior of substances calculate the volume etcetera.

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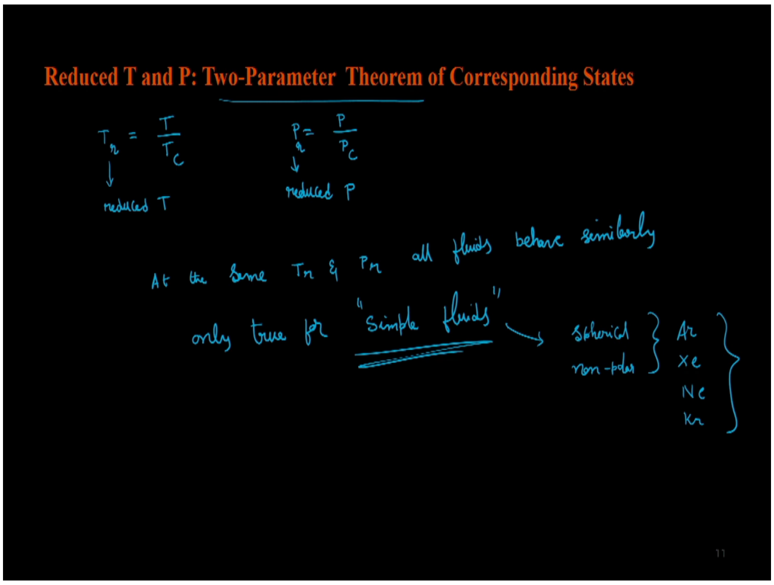

Reduced T and P: Two-Parameter Theorem of Corresponding States

$T_r = \frac{T}{T_c}$ ↓ reduced T

$P_r = \frac{P}{P_c}$ ↓ reduced P

At the same T_r & P_r all fluids behave similarly

only true for "simple fluids" → Spherical, non-polar } Ar, Xe, Ne, Kr

Now, as you have seen earlier the van der Waals equation of state improves the prediction over the ideal gas behavior. But, still there are there is some discrepancy between what it predicts and what the real experiments yield. This is partly due to assuming that all fluids are going to behave in the same way. And, to be able to better understand that let us talk about what is known as a two parameter theorem of corresponding states.

The underlying assumption in this two parameter theorem of corresponding states is that at the same reduced conditions and by the reduced conditions we mean how far away we are from the critical conditions. So, to be able to define how far away we are from critical conditions, we are going to define two variables T r the reduced temperature and P r the reduced pressure which is the ratio of the actual temperature to critical temperature, actual pressure to critical pressure. This is called as the reduced temperature and this is called as the reduced pressure right.

So, the two parameter theorem of corresponding stage simply says that at the same T r and P r all fluids behave in the same way, which means their molar volumes are going to be similar. The other thermodynamic properties are going to be similar of course, in real life this is not true. What was found is that this behavior is predicted well with T r and P r only for simple fluids. And, by simple fluids we mean fluids which are fairly spherical, right they are fairly non-polar.

So, fluids such as argon, it is a noble gas and its fairly spherical molecule xenon, neon things such as these may be assumed to be simple fluids. And, for simple fluids the two parameter theorems of corresponding states seems to pretty well; the simple fluids pretty much obey this two parameter theorem of corresponding states. On the other hand fluids are also known to have fair bit of polarity such as water and there are not spherical molecules; they might be linear molecules such as CO 2 etcetera. So, these fluids do not follow the two parameter theorem of corresponding states strictly.

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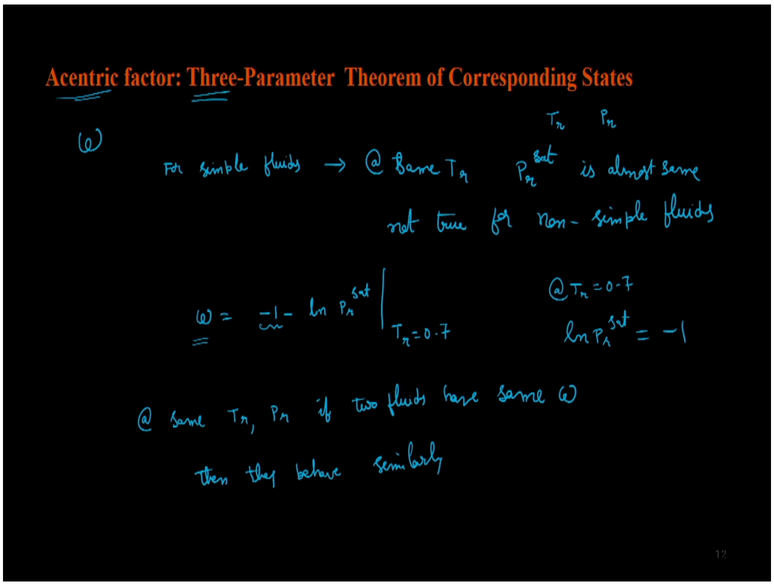

Acentric factor: Three-Parameter Theorem of Corresponding States

T_r P_r

ω

For simple fluids → @ same T_r P_r^{sat} is almost same

not true for non-simple fluids

$$\underline{\underline{\omega}} = \underset{\sim}{-1} - \ln P_r^{sat}\Big|_{T_r=0.7}$$

@ $T_r = 0.7$

$\ln P_r^{sat} = -1$

@ same T_r, P_r if two fluids have same ω

then they behave similarly

And additional parameter has been introduced to calculate to characterize such fluids to account for their polarity, to account for the difference in their sizes etcetera. And, the way we do we introduce this third parameter in the theorem of corresponding states is by introducing what is known as acentric factor denoted by the Greek letter omega. This acentric factor simply turns out to be the difference in the now, remember the two parameter theorem of corresponding states says that at the same T r and P r all fluids have to behave similarly which means their molar volumes also have to be same etcetera.

Now, if it is a saturated fluid then given a T r all fluids should have the same P r which actually turns out to be not true for polar fluids for non-simple fluids even if the T r is same then P r is not same. For simple fluids right at same T r the reduced vapor pressure or the reduced saturation pressure is almost same. However, this is not true for non-simple fluids. And this difference between the vapor pressures of simple fluids and non-simple fluids is used as a measure of non-simplicity right.

So, we call that as the acentric factor we take the difference in the vapor pressures and this needs to be taken at a convenient T r right. So, we take it at a T r of 0.7 and it turns out at this T r of 0.7 the logarithm of P r sat for simple fluids is negative 1. So, that is where we get negative 1 here and then the logarithm of P r sat for non-simple fluids and this difference is what we call as omega right. So, we call this omega as the acentric factor and now at same T r and P r; if two fluids have same omega then they behave similarly. This is how we read the three parameter theorem of corresponding states.

So, not just having T r and P r to be same is enough. We also need to ensure that the fluids have same values of acentric factor then they are going to behave similarly; if not obviously, they are going to behave differently.

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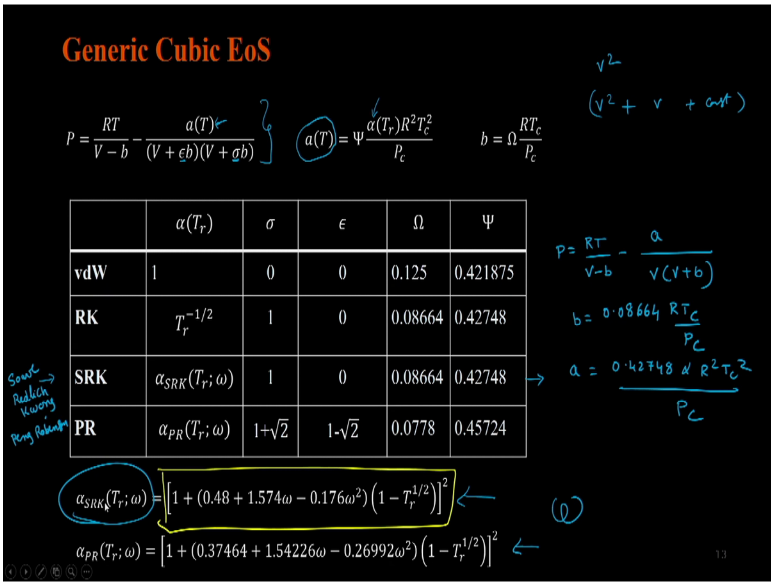

Generic Cubic EoS

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\underline{\epsilon} b)(V+\underline{\sigma} b)} \qquad a(T) = \Psi \frac{\alpha(T_r) R^2 T_c^2}{P_c} \qquad b = \Omega \frac{RT_c}{P_c}$$

v^2

$(v^2 + v + \text{cnst})$

	$\alpha(T_r)$	σ	ϵ	Ω	Ψ
vdW	1	0	0	0.125	0.421875
RK	$T_r^{-1/2}$	1	0	0.08664	0.42748
SRK	$\alpha_{SRK}(T_r;\omega)$	1	0	0.08664	0.42748
PR	$\alpha_{PR}(T_r;\omega)$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.0778	0.45724

Soave → Redlich Kwong

Peng Robinson

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)}$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

$$a = \frac{0.42748\, \alpha\, R^2 T_c^2}{P_c}$$

$$\alpha_{SRK}(T_r;\omega) = \boxed{\left[1 + (0.48 + 1.574\omega - 0.176\omega^2)\left(1 - T_r^{1/2}\right)\right]^2} \leftarrow$$

ω

$$\alpha_{PR}(T_r;\omega) = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)\left(1 - T_r^{1/2}\right)\right]^2 \leftarrow$$

Now, the van der Waals equation of state does not involve acentric factor. So, when people developed other equations of state they have tried to bring in the concept of acentric factor. And, in general a cubic equation of state may be written in this form. It is similar to van der Waals equation of state, if you look at it P is R T by mean minus b minus a by something V squared term. It is a quadratic expression in V, but then there might be additional terms; for van der Waals equation of state this term is 0, this term is 0. So, it is simply a by V squared right and also a is a constant for van der Waals equation of state.

But, for a general cubic equation of state a does not have to be constant; it might be a function of temperature. And, the quadratic term there might be additional terms after the quadratic term instead of V square as you see here we have additional term in terms of V and a constant in the denominator over here for a general cubic equation of state. This is summarized in this table, we have sigma and epsilon values which are 0 for van der Waals equation of state which may not be 0 for other cubic equations of state. There are several cubic equations of state we have just focusing on three or four important ones for chemical industry which are more popular right. Then the additional thing in here is that the parameter a for the cubic equation of state itself might actually depend on temperature.

For van der Waals it is independent for other cubic equations of state, it might be dependent on temperature as well as this alpha term as you see here which may depend on the acentric factor omega which we have just introduced right. So, we can take this table as a working template depending on what cubic equation of state we want to use. We can reduce the form of the cubic equation of state calculate the other parameters and try to write what we are interested in. For example, if I have to simplify use this template and write an expression for this is saw a Redlich Kwong equation of state, RK is Redlich Kwong, SRK is Soave Redlich Kwong equation of state right and this is Peng Robinson equation of state etcetera.

Now, if I want to write the expression for Soave Redlich Kwong equation of state it would read as P is R T by V minus b minus a by notice that sigma is 1 epsilon is 0. So, it will be V V plus b that would be expression cubic equation of state expression and b is going to be omega. For SRK the value of omega is 0.08664 R T c over P c and a is phi which is 0.42748 alpha R squared T c squared over P c. And, the alpha itself is given by this expression in terms of the reduced temperature and the acentric factor. So, the alpha itself for this particular equation of state is given by this expression.

So, once I have the acentric factor and the temperature and hence the reduced temperature I can calculate alpha go back and plug it in here to calculate a, b and whatever is needed out of the equation of state alright. So, let us see how we can use this particular type of equations of state; we will just solve one or two quick examples based on these ideas.

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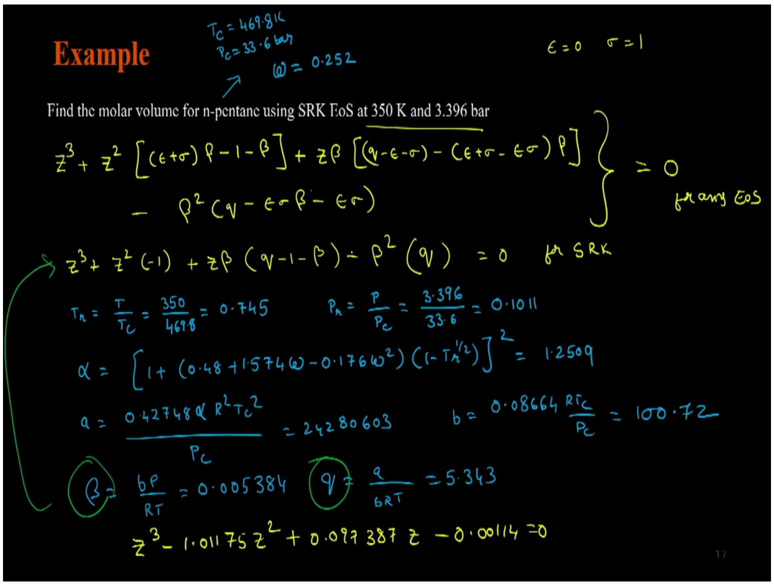

Example

$T_c = 469.8\,K$

$P_c = 33.6$ bar

$\omega = 0.252$

$\epsilon = 0 \quad \sigma = 1$

Find the molar volume for n-pentane using SRK EoS at 350 K and 3.396 bar

$$\left.\begin{array}{l} z^3 + z^2\left[(\epsilon+\sigma)\beta - 1 - \beta\right] + z\beta\left[(q-\epsilon-\sigma) - (\epsilon+\sigma-\epsilon\sigma)\beta\right] \\ \quad - \beta^2(q - \epsilon\sigma\beta - \epsilon\sigma) \end{array}\right\} = 0$$

for any EoS

$$z^3 + z^2(-1) + z\beta(q - 1 - \beta) - \beta^2(q) = 0 \quad \text{for SRK}$$

$$T_r = \frac{T}{T_c} = \frac{350}{469.8} = 0.745 \qquad P_r = \frac{P}{P_c} = \frac{3.396}{33.6} = 0.1011$$

$$\alpha = \left[1 + (0.48 + 1.574\omega - 0.176\omega^2)(1 - T_r^{1/2})\right]^2 = 1.2509$$

$$a = \frac{0.42748\alpha R^2 T_c^2}{P_c} = 24280603 \qquad b = 0.08664\frac{RT_c}{P_c} = 100.72$$

$$\beta = \frac{bP}{RT} = 0.005384 \qquad q = \frac{a}{bRT} = 5.343$$

$$z^3 - 1.01175z^2 + 0.097387z - 0.00114 = 0$$

So, we want to find the molar volume for n pentane using SRK equation of state at 350 Kelvin and 3.396 bar; similar to what we have done in the previous problem, but this time we are going to use a different equation of state alright. So, to be able to do that the first thing we want is to be able to identify the equation we want to solve. Let say it is similar to the cubic expression in the compressibility factor for van der Waals equation; I want to solve the cubic expression for the SRK equation of state. For any generic cubic equation of state the cubic in z it turns out is going to be z cube plus z squared epsilon plus sigma times beta minus 1 minus beta plus z times beta q minus epsilon minus sigma minus the constant term beta square q minus epsilon sigma beta minus epsilon sigma.

This equals 0, this is a simplified version for a generic cubic equation of state. Now, for SRK equation of state remember that we said epsilon is 0 sigma is 1 for SRK. So, we can plug that in and this reduces to z cube plus epsilon and sigma are 0 and 1 right plus z squared into minus 1 plus z times beta q minus 1 minus beta q minus 1 minus beta minus beta squared q equal to 0. This would be for SRK equation of state, this would be for any equation of state. So, with just simplified the expression in the cubic expression in the compressibility factor. Now, we want to solve this cubic expression in terms of the compressibility factor.

But, the first thing I want to do is find out what the values of the parameters for this equation of state are going to be right. And, remember we said that I am interested in the critical parameters for n pentane. I am going to go back to the handbook and find out what the critical parameters are, we have already looked at the two of them. T c was 469.8 Kelvin P c was 33.6 bar and the other parameter I need is the acentric factor or omega for this guy and pentane it turns out to be 0.252. Now, once I have these values I can first go and calculate the reduced conditions T r which is T over T c. So, that is 350 over 469.8 which turns out to be 0.745.

And, the reduced pressure which is P over P c right P over P c that turns out to be 3.396 over 33.6 which is 0.1011. Once I have the reduced temperature and pressure I can go back and calculate alpha which is 1 plus 0.48 plus 1.574 omega. Now, we remember this is the expression for alpha for SRK equation of state 1 minus T r to the power half whole squared; I know omega I know T r. So, I should be able to calculate this alpha straightforward in the straightforward manner 2509. And because now, I have alpha I can calculate a which happens to be 0.42748 alpha R squared T c squared over P c which is 24280603. And, b happens to be 0.08664 R T c over P c which happens to be 100.72.

And, once I have a and b I can calculate beta which is b P over R T which is 0.005384 in this case and q which is a by b R T which is 5.343. Now, once I have all these numbers I have beta, I have q that is all I need; once I have beta and q I can go back and put in this equation to get the final cubic expression in terms of z. And, it turns out that expression is z cube minus 1.01175 z squared plus 0.097387 z minus 0.00114 is 0.

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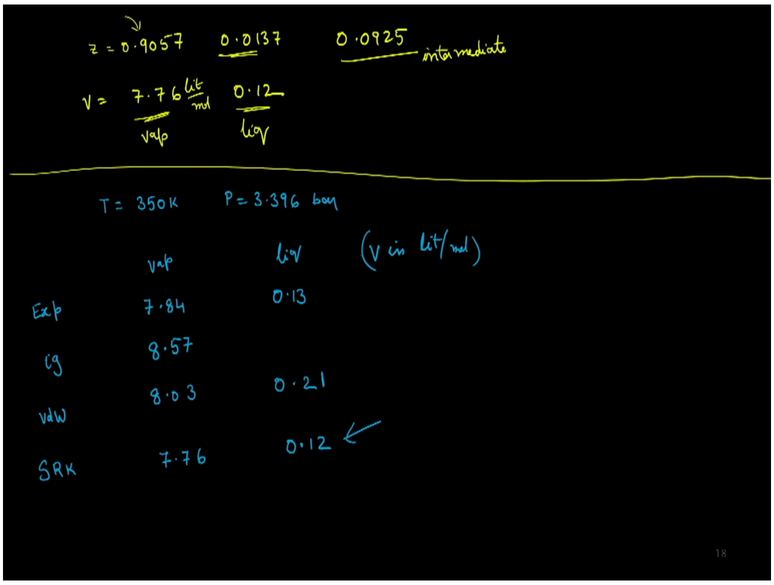

z = 0.9057   0.0137   0.0925 intermediate

V = 7.76 lit/mol   0.12

vap   liq

T = 350 K   P = 3.396 bar

	vap	liq (V in lit/mol)
Exp	7.84	0.13
ig	8.57	
vdW	8.03	0.21
SRK	7.76	0.12

So, this is the cubic in z I want to solve using SRK equation of state; at this condition right also z values I get are 0.9057 0.0137 and 0.0925. And, the corresponding values for volume I get are 7.76 and 0.12. Remember this is closer to 1 so, this is the gas phase volume litres per mole. This is the gas phase volume or the vapor phase volume and this one is the smallest of the roots. So, this will give me the liquid phase volume. This is the intermediate root which has no physical significance for now.

So, we have solved the molar volumes for n pentane at a given temperature and pressure using SRK equation of state. Now, if you recall in one of the earlier problems we have used a van der Waals equation of state. The temperature is 350 Kelvin and the pressure is 3.396 bar and I have this happens to be in a two phase region. The experimental values for n pentane at these conditions is 6.84 7.84 and 0.13. The van der Waals equation of state values I am sorry this is the vapor phase and this is the liquid phase right. This is the vapor phase and this is the liquid phase volume V in litres per mole.

Now, if you recall ideal gas predicts only the vapor phase volume; obviously, and the ideal gas prediction is 8.57 about a good 10 percent off from the reality. When I used van der Waals equation of state I can predict both the vapor and the liquid phase volumes. And, the values I predicted were 8.03 and 0.21. The vapor phase volume improved and I can also predict a liquid volume, but still the liquid phase volume is fair bit off from experiments vapor phase volume is getting. Or, I can if I used SRK equation of state actually the prediction is much better right. I also have remember I also have an additional parameter in terms of the acentric factor.

The prediction improved in this case and I predict 7.76 much closer to the experimental value and 0.12 again much closer to the experimental value. So, in this case the SRK equation of state does much better. Now, remember there is no single equation of state that can predict behavior of all the fluids. One has to match what the equation of state predicts with what the experimental behavior is to be able to say that, within this region this particular equation of state is going to predict the behavior better etcetera. In summary what we have done today is looked at a cubic equation of state. And, how I can calculate both the vapor and liquid volumes for using this particular cubic equation of state, that is all for today.

Thank you.