Advanced Thermodynamics
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Lecture – 15
Fugacities in Gaseous Mixtures - 2

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is fugacities in gaseous mixtures part 2. So, we have been discussing different types of equations of state and then their connection with intermolecular potentials, etc., and then we also seen how to obtain the fugacity coefficient of a component i in the mixture or a fugacity coefficient of pure component, etc., those relations and all that we have seen and then we have seen that most of these equations of state, either equations of state you call or intermolecular potentials you take or you take the fugacity expression that finally you got, they are having some kind of limitations.

One or other kind of limitations, maybe valid at moderate densities, etc., those kinds of things or limitations may be having, right? So, now, what we do? We go further in details to find out fugacities in gaseous mixture, especially at higher densities, right? So, that is what we are going to discuss, how to take care of fugacities of a component in a mixture, especially if the mixture is of a higher density, those kinds of things we are going to see now, right?

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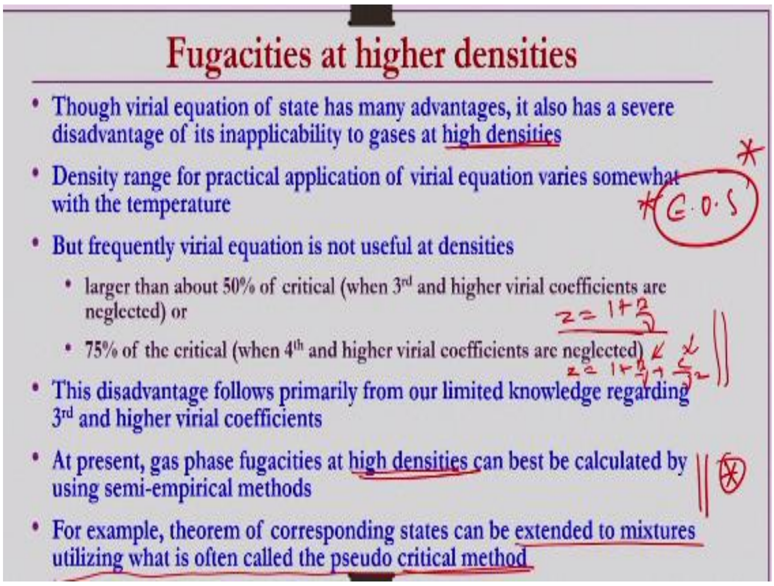

Fugacities at higher densities

- Though virial equation of state has many advantages, it also has a severe disadvantage of its inapplicability to gases at high densities
- Density range for practical application of virial equation varies somewhat with the temperature
- But frequently virial equation is not useful at densities
  - larger than about 50% of critical (when 3rd and higher virial coefficients are neglected) or
  - 75% of the critical (when 4th and higher virial coefficients are neglected)
- This disadvantage follows primarily from our limited knowledge regarding 3rd and higher virial coefficients
- At present, gas phase fugacities at high densities can best be calculated by using semi-empirical methods
- For example, theorem of corresponding states can be extended to mixtures utilizing what is often called the pseudo critical method

*E.O.S

$z = 1 + \frac{B}{v}$

$z = 1 + \frac{B}{v} + \frac{C}{v^2}$

We have already seen that virial equation of state that we have been discussing for quite a few lectures for last couple of weeks, right? We understand that this is one of the best equation of state especially because of the reason that the coefficients or the constants associated with the equations of state, the virial equation of state, are directly having a relation with intermolecular potential of species that we have taken that is one advantage. Another advantage is that we do not need any kind of mixing rules in order to find out this coefficient for the mixture, right?

So, because of these advantages, we realize that it is one of the best equation of state that is available, right? But again it is also having some kind of disadvantages. Disadvantages something like that it is valid only at low to moderate densities only, it is not validated higher densities, right? So, that is one of the disadvantages. So, though virial equation of state has many advantages, it has also a severe disadvantage of its inapplicability of gases at high densities that is what we have already seen, right?

For that the density range for practical applications of virial equation is again dependent on the range of temperature because virial equation of state if you see these virial coefficients are the functions of temperature only. But they are independent of pressure or densities those coefficient, but the density of a system that depends on the range of temperature. So, we cannot specify directly under what range of temperature these equations are going to be a kind of better equations, under what range these equations are going to be not good one such kind of specifications we cannot make based on the temperature.

That is the reason we are making this based on the densities because densities are directly related to the temperature and the second and third virial coefficient, whatever the coefficients of this virial equation of state are there, they are again function of temperature. Since these coefficients are function of temperature, so rather saying that this equation of state is valid for certain low temperature or certain high temperature rather saying that one, we are saying in terms of densities because density is directly related to the temperature and the temperature is affecting these virial coefficients, okay?

It has been found that frequently it has been observed that virial equation of state is not useful especially when the density of the mixture is larger than about 50 % of the critical density, then under such conditions usually third and higher virial coefficients are neglected and then when you use only this $z = 1 + \frac{B}{v}$, up to this part only that is up to second virial coefficient only, then obviously it is not going to give a kind of a reliable information.

Similarly, even though if the densities are up to 75 % of the critical density, then even if you have including this third virial coefficient also, then also the results are not going to be much reliable compared to the experimental results, right? So, even as you go towards the more closer and closer by critical density, critical point, then what happens you know, the reliability of this even virial equation is going to decrease even when you have a kind of up to third virial coefficient also included in the equation.

Then we know that these constants B and C that second and third virial coefficient, data is available sufficiently for second virial coefficient, but third virial coefficient data is very scarcely available even for pure components, right? Because of such limitations, first of all data is limited for the third virial coefficient, even if the data is available and then you include the third virial coefficient or up to the third virial coefficient term in the virial equation and do the calculations, you may not get appropriate results by virial equation of state.

Appropriate in the sense matching with experimental results when the density of the mixture is almost up to 75 % of its critical value, right? So, then what you may think if the density is even less than that at the critical point, then let us say even if you go up take only 50 % of the critical density, then what happens? Then also if you take only up to the second virial coefficient, then again the accuracy of the results obtained by the virial equation of state is not going to be good enough especially when compared to the experimental results.

So, these are the important points one has to keep in mind and then why we have to keep in mind these points because we have already seen in one of the lectures, the equation of state, the reliability or the suitability of equation of state or superiority of any equation of state depends on how much it is matching with the experimental results, especially at or near critical point, okay? If the results obtained, thermodynamic properties obtained by equation of state are matching with experimental results at the conditions which are close or at the critical point.

At critical conditions or near critical conditions if the thermodynamic properties obtained by equation of state are matching with experimental results, then you can say such equation of state are going to be much more reliable than the others, that is what we have seen. Why is this problem is coming, especially at critical or near critical point? Because what happens, the properties near critical point changes drastically with slight change in the temperature or pressure something like that.

Because of such reasons, we cannot have a kind of equation of state which may be covering the whole range of low temperature, low pressure to the high temperature, high pressure crossing this critical temperature critical point, etc., those kind of thing. So, because of such reasons, the validity of any equation of state depends on how good it predicts the experimental results at critical or near critical point conditions.

Let us say if you have the system at around 50 ℃. Then if you increase the temperature to the 50 to 55 ℃, then density may not vary much, dielectric constant of the system may not very much, right? But the same system you take and then your operating temperature is near the critical condition, let us say critical point for fluid is around 370 ℃. So, critical temperature is 370 ℃ and then for the same fluid for the same system if you measure the variation in the density at this 370 ℃.

If you decrease this temperature from 370 to 365 ℃ just by decreasing by 5 ℃ or if you increase this temperature 370 to 375 ℃ thus just increasing by 5 ℃, the density is going to be vary much more drastically. So, because of that reasons, one cannot have a kind of equation state which may account for such kind of drastic changes in the properties. That is the reason you know many of the equations of state are not valid at a critical point conditions for many cases, okay?

So, that is the reason this validity of any equation of state has been demonstrated by comparing the results obtained by such equation of state at critical conditions by comparison with the experimental results. So, that is the reason this critical point has been taken as a kind of reference point for establishing the reliability of any equation of state. In other words if the experimental results at critical point can be reproduced by any equation of state at critical condition, then we can say that particular equation of state is going to be much more reliable than any other equation of state.

So, further obviously, this disadvantage follows primarily from our limited knowledge regarding the third and higher virial coefficient. As I already mentioned, the available data for a second virial coefficient is sufficiently there, but third and higher virial coefficient the data or available data is very scarce. So, but at present, gas phase fugacities at high densities can be best calculated by using semi-empirical methods. So, this actually we have discussed all these, how, what is this method, etc., how to apply for this mixing rule, etc.

When we find out the fugacity of the component in mixture, those kind of things we have seen but without discussing much details why are we using that one. So those principles we are using it. Basically at higher densities, we are going to use an approach which is called as a kind of semi-empirical methods which we have already used for the few cases, but without understanding what is this semi-empirical method. So, those things we are going to see now. For example, theorem of corresponding states can be extended to mixtures utilizing that it is often called a pseudocritical method.

If you recollect the corresponding states theory, whatever the corresponding states theory that derivations, etc., we have done for the equation of state or you know developing a kind of equation of state in reduced coordinates which is kind of universal function for all the gases which obey that particular equation of state, right? So, let us say Van der Waal's equation of state is obeyed by many gases.

So, we have developed a kind of a universal function or universal Van der Waal's equation of state in terms of reduced temperature and reduced pressure which is going to be same for all fluids, which are obeying the Van der Waal's equation of state including those constants. Those constants are related to the critical temperature and critical pressure as we have already seen. So, all those things have been done for a kind of pure components, for a kind of pure components only that corresponding states theory.

Whether it is 2 parameters corresponding state theory or you know higher parameter corresponding theory or extended corresponding state theory, they are valid for the pure component. For those pure components only we have developed, but this semi-empirical methods or which is also known as the pseudocritical method, according to this one, this theory can also be extended to mixtures.

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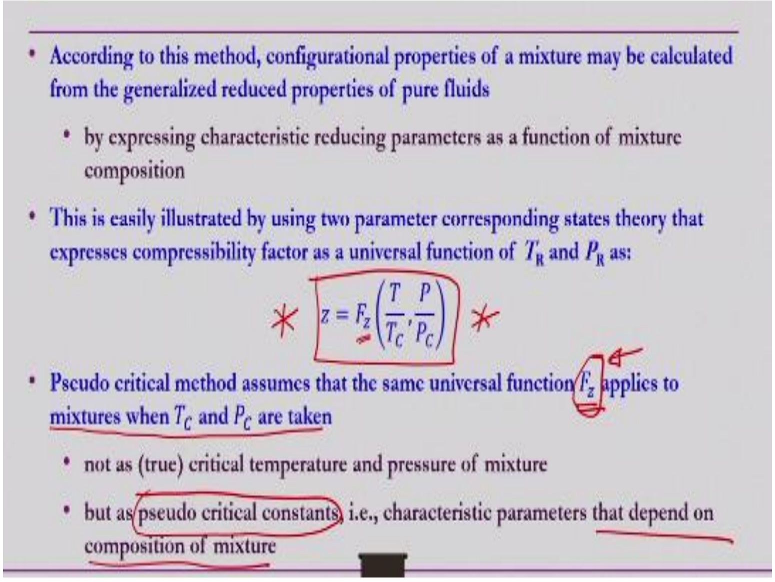

- According to this method, configurational properties of a mixture may be calculated from the generalized reduced properties of pure fluids
  - by expressing characteristic reducing parameters as a function of mixture composition
- This is easily illustrated by using two parameter corresponding states theory that expresses compressibility factor as a universal function of T_R and P_R as:

$$* \boxed{z = F_z\left(\frac{T}{T_C}, \frac{P}{P_C}\right)} *$$

- Pseudo critical method assumes that the same universal function F_z applies to mixtures when T_C and P_C are taken
  - not as (true) critical temperature and pressure of mixture
  - but as pseudo critical constants, i.e., characteristic parameters that depend on composition of mixture

According to this method, configurational properties of a mixture may be calculated from the generalized reduced parameters or reduced properties of pure fluids by expressing characteristic reducing parameters as a function of mixture composition. So, whatever these reduced parameters of pure fluids are there that are going to be generalized one and these generalized ones are expressed by characteristic reducing parameters, which are again functions of composition of the mixture, this is what it says.

This is easily illustrated by using 2 parameter corresponding state theory that expresses compressibility factor as universal function of reduced temperature and reduced pressure as $z = F_Z\left(\frac{T}{T_c}, \frac{P}{P_c}\right)$, right? So, here pseudocritical method assumes that these same universal function F_Z applies to the mixture also, right? Actually as per the corresponding state theory whatever the z as function of T_R, P_R or $\frac{T}{T_c}, \frac{P}{P_c}$, this is valid for the pure components.

But according to this pseudocritical method or semi-empirical method, what we can say this universal function F_Z whatever is there it is also applicable to mixtures also, but when this T_c and P_c are taken not as a kind of true critical temperature, critical pressure of the mixture, but as some kind of composition dependent constants. Then we can say this particular thing is also valid, this particular corresponding theory or this particular universal function whatever is there for compressibility that is also going to be valid for mixtures by taking this T_c and P_c are not as a true critical temperature and true critical pressure of the mixture.

But rather as a pseudocritical constant that is characteristic parameters that depend on the composition of the mixture, pseudocritical constants. So, that is the reason this method is also known as the pseudocritical method, okay? So, now it says whatever the T_c and P_c of the mixture are there, they are dependent on the composition. So, how are they dependent? What is the function between T_c and composition and then P_c and composition? Is it a linear or non-linear? That again has to be answered appropriately.

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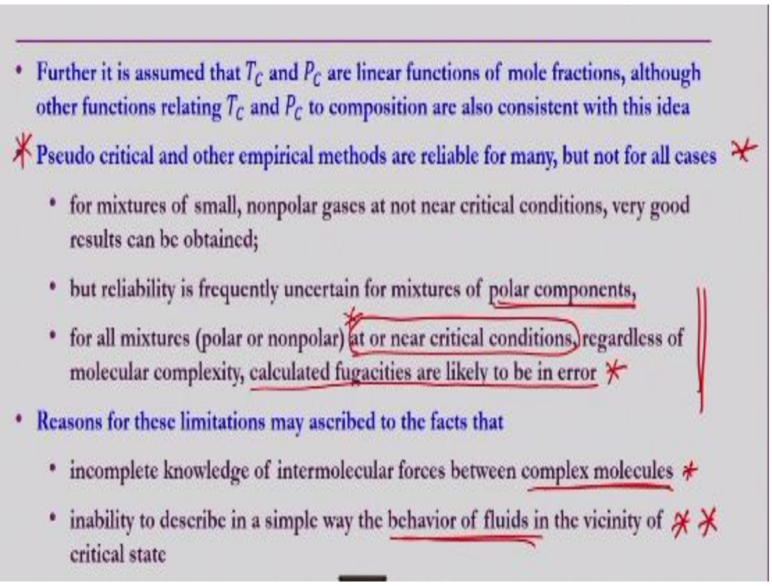

- Further it is assumed that T_C and P_C are linear functions of mole fractions, although other functions relating T_C and P_C to composition are also consistent with this idea
- Pseudo critical and other empirical methods are reliable for many, but not for all cases
  - for mixtures of small, nonpolar gases at not near critical conditions, very good results can be obtained;
  - but reliability is frequently uncertain for mixtures of polar components,
  - for all mixtures (polar or nonpolar) at or near critical conditions, regardless of molecular complexity, calculated fugacities are likely to be in error
- Reasons for these limitations may ascribed to the facts that
  - incomplete knowledge of intermolecular forces between complex molecules
  - inability to describe in a simple way the behavior of fluids in the vicinity of critical state

Further in this method according to pseudocritical method, it is assumed that the T_c and P_c are linear functions of mole fractions, although other functions relating T_c and P_c to composition are also consistent with this idea, okay? Though this method whatever the pseudocritical method that is there for the mixtures are the method which we are calling as a pseudocritical method, it says that the universal function F_z of compressibility which is valid for pure component is also valid for a mixture of those components.

But only thing that the critical temperature and critical pressure of these mixtures are composition dependent ones and then they are linearly dependent on the combination. But however, it has been found that this relation between the critical parameters and composition though if it is not linear, then also it has found that the results are consistent with this particular idea of a pseudocritical method, okay? Pseudocritical method and other empirical methods are reliable for many cases, but not for all cases, okay?

Let you have n number of mixture, n number of or n combinations of mixtures of several gases, then you can find this pseudocritical method may be suitable for many cases, but one cannot guarantee that this method is going to be useful for all cases. These observations are by experimental reliability or by matching with experimental results. Let us say we have a corresponding state theory, you apply this corresponding states theory to the mixtures because the original corresponding state theory is developed for the pure fluids.

Now, we are making a kind of pseudocritical parameter estimation by finding this T_c and P_c as functions of composition. Now, using this T_c and P_c as function of composition of the mixture, we apply the same corresponding state theory to the mixture, then we call it as a kind of pseudocritical theory, okay? So, it has been found when we apply this pseudocritical method, it has been found that it is reliable or applicable for many cases, but not all cases. Obviously, we can understand when it is going to be reliable or provides a good approximation or satisfactory comparison with experiments.

So, what we can understand clearly we have been seeing that for the small simple non-polar gases many things are again simple and straightforward. So, under such conditions, this pseudocritical method is also expected to perform well and it has been found by experimentally the same thing that is for mixtures of small non-polar gases at not near critical conditions, okay? Slightly away from the critical condition.

For mixtures of small and non-polar gases, it has been found that whatever the results obtained by the pseudocritical method are there, they are providing very good results compared to the experimental ones, but reliability is frequently uncertain for mixtures of polar components. Polar components even for the pure components several difficulties are there, you know very few models, etc., are available.

So, again if such a less accurate approach for pure component is there for a polar component, but the same less accurate polar components approach whatever is there the corresponding sates theory, then if the same thing if you apply for the mixture of polar components, it is going to be uncertain, it is not going to be certain, right? So, we have seen that for polar component, this acentric factors etc., all those things are coming into the picture, especially for non-spherical or larger polar molecules, right?

So, when we brought in additional things into the corresponding theory, we found it even for pure components, but if the component is polar component the reliability is very less, is not that good, right? If for pure component the reliability is not good, so obviously that approach is not going to be match well, may not provide certain reliable information for mixtures when you apply this pseudocritical method.

Further for all mixtures, whether it is polar or non-polar, at or near critical conditions regardless of molecular complexity, whether the simple spherical molecules, non-spherical molecules, whatever the calculated fugacities are there they are likely to be in error. So, one thing is clear that from this pseudocritical method is not going to be useful for the cases if the mixture is at the conditions of close to the near critical conditions or close to the critical conditions, right?

So, that means this pseudo empirical method can be used as a kind of a first order approximation for simple non-polar molecules at conditions away from the critical conditions. If you take the system closer and closer to the critical conditions, whether the molecules are simple or non-simple or complex molecules whatever you take, the reliability is going to be questionable. So, why this inconsistency even for small molecules if we go towards the critical conditions? So there must be a reason. So, there are 2 reasons.

First reason is that for complex molecules, intermolecular forces, the information or knowledge about intermolecular forces is very small that is one reason, but most important reason is that at critical conditions or near critical conditions, we are unable to predict the behavior of fluids in a simple and easy manner. That is the important thing that because of this reason we are not able to get the reliability which is missing at or near critical condition because we are unable to describe the behavior of fluids in the vicinity of the critical state.

Why because as I already mentioned at the critical state even if the temperature, pressure changes slightly, as I mentioned if the temperature let us say changes, increases or decreases by 5 °C or even sometimes 2-3 °C near the critical condition, then these properties such as density, dielectric constant, etc., are going to vary drastically, they may increase or decrease depends on the system, right?

So, such kind of sharp changes in the properties because of small changes in the temperature or pressure near critical conditions are not able to be captured by existing equations of states. So, that is the reason these problems are existing, okay? That is the reason reliability is questionable, especially at higher densities if you do not use appropriate cases, appropriate expressions or appropriate methods.

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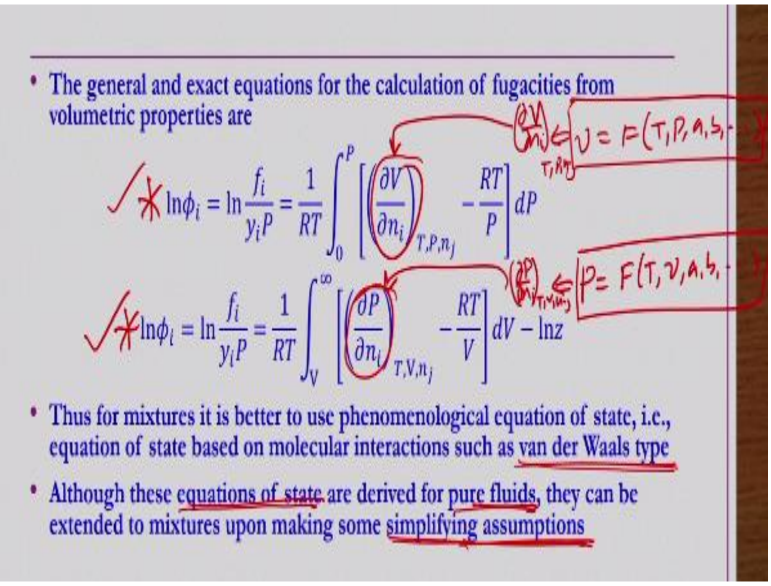

- The general and exact equations for the calculation of fugacities from volumetric properties are

$$\ln\phi_i = \ln\frac{f_i}{y_i P} = \frac{1}{RT}\int_0^P \left[\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} - \frac{RT}{P}\right] dP$$

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} \Leftarrow V = F(T, P, a, b, \ldots)$$

$$\ln\phi_i = \ln\frac{f_i}{y_i P} = \frac{1}{RT}\int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dV - \ln z$$

$$\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} \Leftarrow P = F(T, V, a, b, \ldots)$$

- Thus for mixtures it is better to use phenomenological equation of state, i.e., equation of state based on molecular interactions such as van der Waals type
- Although these equations of state are derived for pure fluids, they can be extended to mixtures upon making some simplifying assumptions

So, now coming to the estimation of fugacities, we have already seen general and exact equations for the calculation of fugacity from volumetric properties. We have these 2 equations. If you have an equation of state in a kind of form that molar volume is one side, then other conditions like temperature, pressure and then constant associated with the equation of state whichever you have taken in order to bring the real behavior, non-ideal behavior of the system, if you write in this particular form, right? Then from here what you can do?

You can find out what is $\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j}$ and then that you can substitute here and then find out the required ln ϕ_i expression that is fugacity coefficient of component i in the mixture by using this expression. Similarly, if equation of state if you write in a pressure explicit form that pressure is one side and then all other terms like the temperature, molar volume, and then constant associated with the equation of state like a, b, etc.

Then from that equation of state again you can find out $\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}$ and then that if you substitute here and then simplify, you can find out what is ϕ_i that is fugacity of component i in the mixture using this expression. These things we have already derived. These things are a generalized expression. These 2 expressions are generalized expression without making any assumption of what kind of equation of state it is, right? So, depending on the equation of state you can find out either $\frac{\partial V}{\partial n_i}$ or $\frac{\partial P}{\partial n_i}$, substitute them here and then find out ϕ_i expression.

Then any equation you use whether this equation you use or you use this equation, you are going to get the same answer for fugacity component i in the mixture, okay? Now, thus for mixtures, it is better to use phenomenological equations of state that is the equation of state based on intermolecular interactions such as Van der Waal's equations, which may bring in the effect of non-ideality in the system appropriately. There are other equations of states are also we have seen, Redlich-Kwong equation, Peng-Robinson equation, etc.

Those kinds of things we have seen, but what we have seen, we have seen these equations are valid for pure fluids only, right? All these equations of state they are valid for the pure fluids only, but it can be extended to mixtures upon making some simplifying assumptions. You can have a kind of some simplifying assumptions and then make a kind of mixing rule to get the equation of state for the mixtures with appropriate constants a, b, etc., for the mixtures, but as we are saying that simplifying assumptions, so these mixing rule are going to have some kind of limitations.

Accordingly there are many mixing rules are available, but we have been using a few mixing rules without knowledge, but mixing rule has to be used with knowledge and then that knowledge may be coming with the experience or maybe by thoroughly understanding the nature of the equation of state and nature of the molecules, etc., and accordingly one has to use which equation of state or which mixing rule is going to be appropriate for a given equation of state for a given system like that one has to make a clear reliable stand before using these equations of state for the mixtures.

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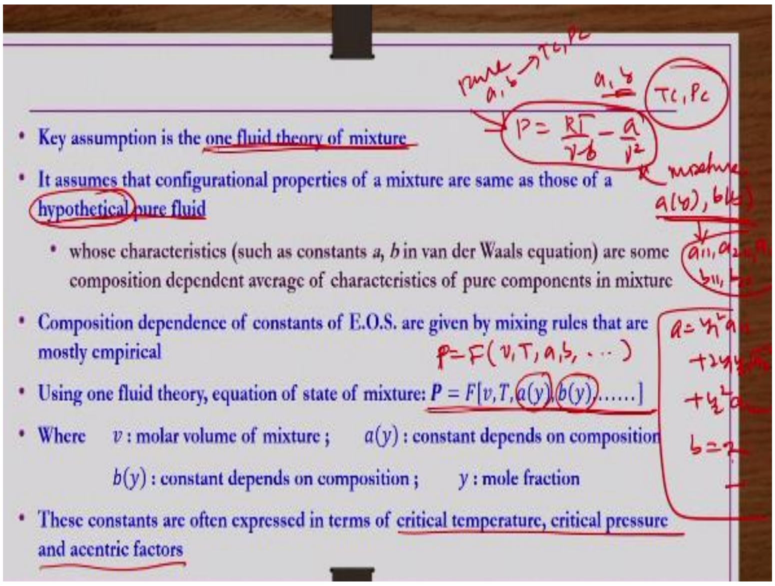

- Key assumption is the one fluid theory of mixture
- It assumes that configurational properties of a mixture are same as those of a hypothetical pure fluid
  - whose characteristics (such as constants *a*, *b* in van der Waals equation) are some composition dependent average of characteristics of pure components in mixture
- Composition dependence of constants of E.O.S. are given by mixing rules that are mostly empirical
- Using one fluid theory, equation of state of mixture: $P = F[v, T, a(y), b(y), \ldots\ldots]$
- Where v : molar volume of mixture ; $a(y)$: constant depends on composition
  $b(y)$: constant depends on composition ; y : mole fraction
- These constants are often expressed in terms of critical temperature, critical pressure and acentric factors

One key assumption is the one fluid theory of mixture. You assume that the mixture is a kind of one fluid, okay? It assumes that the configuration and properties of a mixture are same as those of hypothetical pure fluids. It is not a pure fluid, but hypothetical fluids. So, let us say a, b constants for Van der Waal's equations that we have as functions of T_c and P_c that we have derived, right? So this T_c and P_c for the pure component. So for the pure component, T_c and P_c if you know, then you can find out what is this a, b constant.

Likewise for the mixtures also, you know what are these T_c, P_c by whatever the pseudocritical method that we have been discussing. Then accordingly these a, b be constants can be found for the mixtures also. Now but this method when we have this one fluid theory, what we are assuming? We are assuming that mixture is having is a kind of one fluid rather than treating as a kind of mixture of 2 different or more than one component, 2, 3, or whatever.

It is rather assuming that is a mixture of these many components, you are taking as a kind of one particular fluid and then assuming the properties, the configurational properties of mixture are same as those of a hypothetical fluid for which this a, b relations as function of T_c and P_c are also valid and then whose characteristic constants such as a, b in Van der Waal's equation for example we are taking are some composition dependent average of characteristics of pure components in the mixture, okay?

This is the primary assumption of this one fluid theory of mixture. So, composition dependence of constants of equation of state are given by mixing rules that are again mostly empirical and then using one fluid theory equation of state, we can write it as something like

P = F[T, v, a(y), b(y),….]. If it is pure component, then what we have written, just in the previous slide we have written P = F [T, v, a, b, etc.], this is what we have written.

Now here in the case of mixture, similar form we are writing, but we are writing this a and b are dependent on the composition, so for which we are using mixing rules, okay? Here v is nothing but molar volume of mixture, a(y) is nothing but constant depends on composition, b(y) is also a constant depends on the composition, y is the mole fraction of the system that we have taken and these constants are often expressed in terms of critical temperature, critical pressure, and acentric factor as we already seen in corresponding states theory, right?

So, these are the things that one has to make sure, that is if let us say if you are using same equation of state let us say P = $\frac{\mathrm{RT}}{v-b} - \frac{a}{v^2}$, the Van der Waal's equation of state if you are using for pure components, then a and b should be related to the T_c and P_c of that particular pure component. If you are using for the mixtures, then this a and b are composition dependent constants, that is they are also in addition to this a and b are functions of a_{11}, a_{22} and then a_{12}, b_{11}, b_{22} if it is a binary mixture.

This a and b depends on these things by having some kind of relation with no composition. For example, we have seen a for the mixture is nothing but y_1^2 a_{11} + 2 y_1 y_2 $\sqrt{a_{11}a_{22}}$ + y_2^2 a_{22}, this is what we have seen like this, okay? Similarly b also we have seen a certain kind of mixing rules. So, those mixing rules we have to use for this constant if we are applying this equation of state for the mixtures, okay? So, how to get it done? We take a couple of example problems and then see this.

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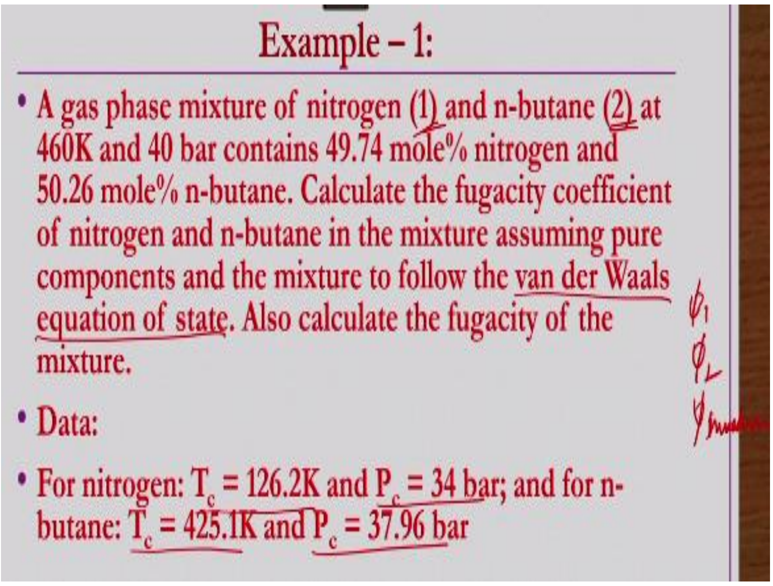

Example – 1:

- A gas phase mixture of nitrogen (1) and n-butane (2) at 460K and 40 bar contains 49.74 mole% nitrogen and 50.26 mole% n-butane. Calculate the fugacity coefficient of nitrogen and n-butane in the mixture assuming pure components and the mixture to follow the van der Waals equation of state. Also calculate the fugacity of the mixture.
- Data:
- For nitrogen: $T_c = 126.2K$ and $P_c = 34$ bar; and for n-butane: $T_c = 425.1K$ and $P_c = 37.96$ bar

ϕ_1

ϕ_2

$\phi_{mixture}$

Example 1. A gas phase mixture of nitrogen which is designated as component 1 and n-butane which is designated as component 2 at 460 Kelvin and 40 bar contains 49.74 mole % of nitrogen and 50.26 mole % of n-butane, almost like we can say 50-50 % mole fractions, right? So, calculate the fugacity coefficient of nitrogen and n-butane in the mixture assuming pure components and the mixture to follow the Van der Waal’s equation of state. Also calculate the fugacity of the mixture, okay?

So, we have to find out ϕ_1 for component 1, ϕ_2 for component 2 and then ϕ for the mixture, okay? So, these are the things we have to find out, f_{mixt} we have to find out. f_1, f_2 also we have to find out. We have to find out first f_1 f_2 and then we can find out whatever the required f_{mixt}, okay? So, we need obviously T_c, P_c data. So, for nitrogen T_c is given, P_c is given, similarly for n-butane also T_c is given and then P_c is given, okay?

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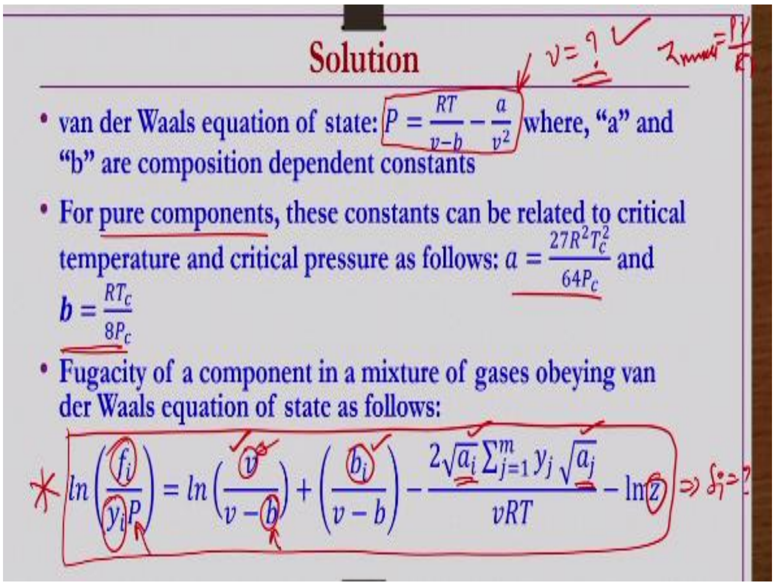

Solution

$v = ?$ ✓ $z_{mixt} = \frac{PV}{R}$

- van der Waals equation of state: $\boxed{P = \frac{RT}{v-b} - \frac{a}{v^2}}$ where, "a" and "b" are composition dependent constants
- For pure components, these constants can be related to critical temperature and critical pressure as follows: $a = \frac{27R^2T_c^2}{64P_c}$ and $b = \frac{RT_c}{8P_c}$
- Fugacity of a component in a mixture of gases obeying van der Waals equation of state as follows:

$$* \boxed{\ln\left(\frac{f_i}{y_i P}\right) = \ln\left(\frac{v}{v-b}\right) + \left(\frac{b_i}{v-b}\right) - \frac{2\sqrt{a_i}\sum_{j=1}^{m} y_j\sqrt{a_j}}{vRT} - \ln z} \Rightarrow f_i = ?$$

So, now we have to find out this thing. So, what we see here Van der Waal's equation of state, we know this is P $= \frac{\text{RT}}{v-b} - \frac{a}{v^2}$ where a and b are composition dependent constants, this we know, okay? For pure components, these constants are related to T_c and P_c as per these equations a = $\frac{27R^2T_c^2}{64P_c}$ and b = $\frac{RT_c}{8P_c}$. These things also we have already derived from the corresponding states theory in one of the previous lecture, okay?

Then fugacity of a component in a mixture of gases obeying Van der Waal's equation of state also we derived, this we derived in the second week of this course, so where we have this expression. What we have done? We have taken a gaseous mixtures having m number of components and not only those individual components, m number of components as well as the mixture obeying the Van der Waal's equation our state. Then for a component i in the mixture, the fugacity coefficient we have already derived in one of the lectures in the second week and that expression is nothing but this one.

So, you need to find out f_1, f_2, right? So, that means if you have to use this equation, y_1, y_2 is given, P is also given, okay? So, now here b is for the mixture. So, for the mixture constant b we have to find out, v is also again for the mixture, so molar volume of the mixture you have to find out. b_i that is b_1, b_2 so that is for the pure component b constant you have to find out and then here a_i a_j that is for the pure component this a_1 a_2 you have to find out, right? Then similarly, a for the mixture also you have to find out and then there is z, z_{mixt} compressibility factor $z_{mixt} = \frac{Pv_{mixt}}{RT}$ also you have to find out.

Then you can substitute all of them here in order to find out what is f_i. So, first what we do? We find out this a_1, a_2 or a_i, a_j and then b_i, b_j we find out. Then we find out this a constant and b constant. Then we will be solving this. Once this a constant and b constant for this Van der Waal's equation of state, then from here you can find out what is v because P and T are all given here, a and b you are just finding out. So, once you find out the v_{mixt}, then you can find out the $z_{mixt} = \frac{Pv}{RT}$.

So once all those things are obtained, we substitute here, so simply you can get fugacity of that particular component or fugacity coefficient of that particular component in the mixture, okay?

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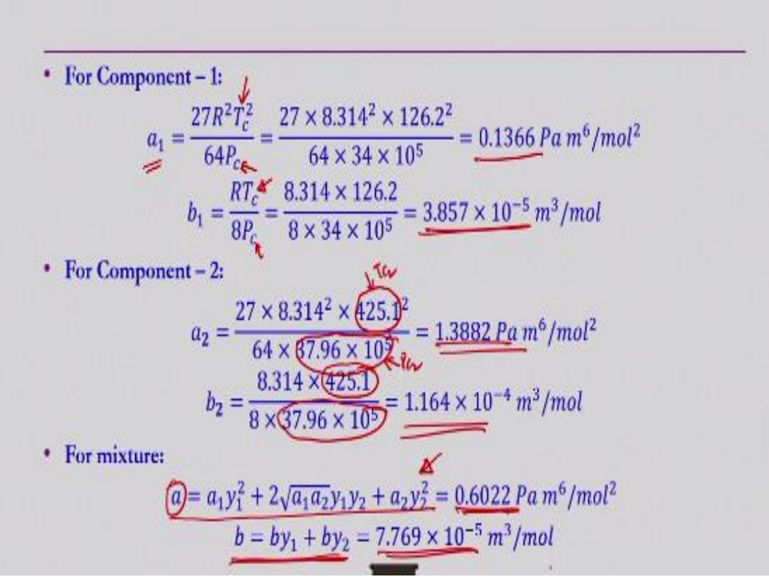

- For Component – 1:

$$a_1 = \frac{27R^2T_c^2}{64P_c} = \frac{27 \times 8.314^2 \times 126.2^2}{64 \times 34 \times 10^5} = 0.1366\ Pa\ m^6/mol^2$$

$$b_1 = \frac{RT_c}{8P_c} = \frac{8.314 \times 126.2}{8 \times 34 \times 10^5} = 3.857 \times 10^{-5}\ m^3/mol$$

- For Component – 2:

$$a_2 = \frac{27 \times 8.314^2 \times 425.1^2}{64 \times 37.96 \times 10^5} = 1.3882\ Pa\ m^6/mol^2$$

$$b_2 = \frac{8.314 \times 425.1}{8 \times 37.96 \times 10^5} = 1.164 \times 10^{-4}\ m^3/mol$$

- For mixture:

$$a = a_1y_1^2 + 2\sqrt{a_1a_2}y_1y_2 + a_2y_2^2 = 0.6022\ Pa\ m^6/mol^2$$

$$b = by_1 + by_2 = 7.769 \times 10^{-5}\ m^3/mol$$

So, first what we do? We find out this constant for component 1.Component 1, I am calling it a_1, b_1. For component 2, I am calling it a_2, b_2. You can also call it as a_{11}, b_{11}, a_{22}, b_{22}. So, now here $a_1 = \frac{27R^2T_c^2}{64P_c}$. This T_c and then P_c now you have to substitute for the component 1 that is for the nitrogen, then you will get a_{11} is this value. Similarly, b_1 or b_{11} if you write it as b_{11} is nothing but $\frac{RT_c}{8P_c}$, here again T_c P_c you have to use for component 1 that is for the nitrogen, then you have b_1 this value, right?

Then for component 2 if you do a_2 similarly, but using here the T_c whatever the T_c information is there that is for the second component T_{c_2}, okay? And then this P_c whatever is there that is also for the second component that is P_{c_2} that is for n-butane, right? Similarly, b_{22} also here, this is for the second component T_c and this is the second component P_c that information is given. So, when you substitute, you will get a_2 and b_2 like this, these numbers, right?

Then we also need for the mixture, for the mixture we know that a = this mixing rule we have been using, indeed that derivation whatever I have shown for ln ϕ_i in the previous expression or $ln\frac{f_i}{y_iP}$ that expression we have, while deriving that expression we needed this a information, so there we have used this mixing rule. So, then we have to use this mixing rule again without any change. So, this is a = y_1^2 a_1 + 2 y_1 y_2 $\sqrt{a_1a_2}$ + y_2^2 a_2, then you have this information.

Then similarly for the b of the mixture, there are several mixing rules are there, we have seen two of them, but in deriving that $ln\frac{f_i}{y_iP}$ expression that I have shown in the previous slide, we have used this mixing rule. So again while solving this problem you have to use this mixing rule only, right? So, in the derivation if you have used this mixing rule, so problem solving also we have to use this one only. So, if you substitute y_1 = 0.4974 and then y_2 = 0.5026, then you get this value for a and b, right?

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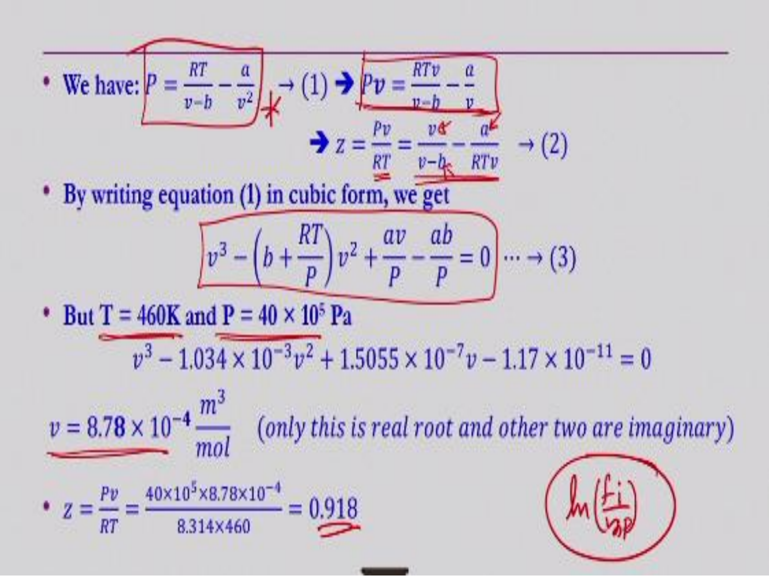

- We have: $\boxed{P = \frac{RT}{v-b} - \frac{a}{v^2}} \rightarrow (1) \Rightarrow \boxed{Pv = \frac{RTv}{v-b} - \frac{a}{v}}$

$$\Rightarrow z = \frac{Pv}{RT} = \frac{v}{v-b} - \frac{a}{RTv} \rightarrow (2)$$

- By writing equation (1) in cubic form, we get

$$\boxed{v^3 - \left(b + \frac{RT}{P}\right)v^2 + \frac{av}{P} - \frac{ab}{P} = 0} \cdots \rightarrow (3)$$

- But T = 460K and P = 40×10^5 Pa

$$v^3 - 1.034 \times 10^{-3}v^2 + 1.5055 \times 10^{-7}v - 1.17 \times 10^{-11} = 0$$

$v = 8.78 \times 10^{-4}\frac{m^3}{mol}$ *(only this is real root and other two are imaginary)*

- $z = \frac{Pv}{RT} = \frac{40\times10^5\times8.78\times10^{-4}}{8.314\times460} = 0.918$

$\ln\left(\frac{f_i}{y_iP}\right)$

Then a and b, a_1, b_1, a_2, b_2, a and b for the mixture we have found. Now we will be finding v_{mixt} and then z_{mixt}, okay? So, if these two also you find, then everything is available to find out the ln ϕ_1, ln ϕ_2. So, this whatever the P = $\frac{RT}{v-b} - \frac{a}{v^2}$ is there, first what I am doing, both the sides I am multiplying by v, then both sides I am dividing by RT, so that I can have $\frac{Pv}{RT}$ = z that can be as a kind of $\frac{v}{v-b} - \frac{a}{RTv}$.

Now, if you have the v_{mixt}, so straightforward $\frac{Pv_{mixt}}{RT}$ if you do, you can get the z_{mixt} or if you use this equation here in the place of here v, you use the v_{mixt} and then here you use b_{mixt} and then here use a_{mixt}, right? So, then that way also you can calculate, any ways possible. So now z_{mixt} you can calculate only when you know the v_{mixt}, v_{mixt} we can calculate from the equation of state, either this equation number 1 or this equation number 2 or any equation you can use it because now we can use any of these equations of this.

We can use this equation of state because you know a and b we have already found for the mixtures. So, everything is known in this equation of state at given temperature and pressure except the molar volume. So, we can expand this equation in the cubic form like this, this also we have done previously, and then solve this equation by substituting T = 460 K and then $P = 40*10^5$ Pascal, these are given, right? Then obviously, when you substitute, a and b you already got, T and P you are substituting this value, R also you know.

So, then this will be a cubic equation in v only, so 3 root should be there. So, out of those 3 roots, you will be having only one real root here and then remaining two are going to be imaginary. So, this is the v_{mixt}, right? So, now once we have the v_{mixt}, so then z_{mixt} can be easily found by $\frac{Pv}{RT}$ expression that is going to be 0.918. So, now in $ln\frac{f_i}{y_iP}$ expression or ln ϕ_i expression that we have seen in the previous slide, everything is not known in the right hand side. So, simply substitute and get ln f_1, ln f_2 values.

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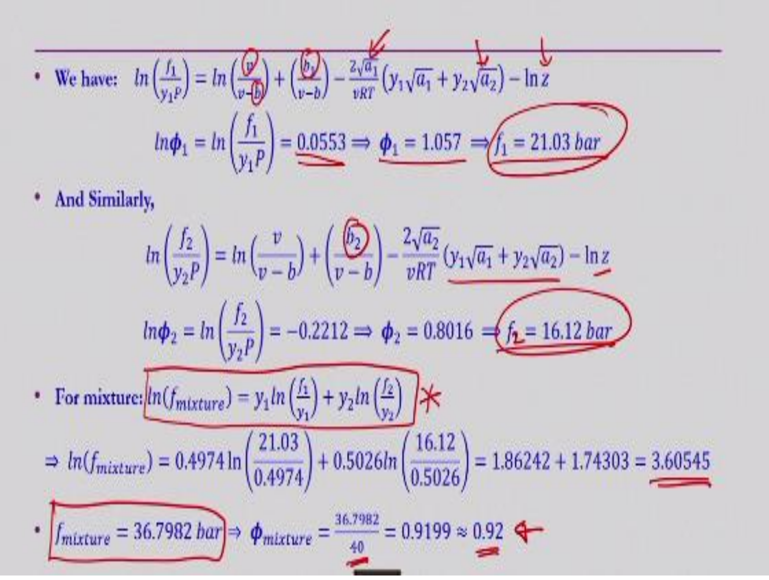

- We have: $ln\left(\frac{f_1}{y_1P}\right) = ln\left(\frac{v}{v-b}\right) + \left(\frac{b_1}{v-b}\right) - \frac{2\sqrt{a_1}}{vRT}(y_1\sqrt{a_1} + y_2\sqrt{a_2}) - \ln z$

  $ln\phi_1 = ln\left(\frac{f_1}{y_1P}\right) = 0.0553 \Rightarrow \phi_1 = 1.057 \Rightarrow f_1 = 21.03\ bar$

- And Similarly,

  $ln\left(\frac{f_2}{y_2P}\right) = ln\left(\frac{v}{v-b}\right) + \left(\frac{b_2}{v-b}\right) - \frac{2\sqrt{a_2}}{vRT}(y_1\sqrt{a_1} + y_2\sqrt{a_2}) - \ln z$

  $ln\phi_2 = ln\left(\frac{f_2}{y_2P}\right) = -0.2212 \Rightarrow \phi_2 = 0.8016 \Rightarrow f_2 = 16.12\ bar$

- For mixture: $ln(f_{mixture}) = y_1 ln\left(\frac{f_1}{y_1}\right) + y_2 ln\left(\frac{f_2}{y_2}\right)$ *

$\Rightarrow ln(f_{mixture}) = 0.4974\ln\left(\frac{21.03}{0.4974}\right) + 0.5026ln\left(\frac{16.12}{0.5026}\right) = 1.86242 + 1.74303 = 3.60545$

- $f_{mixture} = 36.7982\ bar \Rightarrow \phi_{mixture} = \frac{36.7982}{40} = 0.9199 \approx 0.92$

So, $ln\frac{f_1}{y_1P}$ = ln $\left(\frac{v}{v-b}\right)$ + b$_i$ is nothing but now $\frac{b_1}{v-b} - \frac{2\sqrt{a_1}}{vRT}$, $\sum y_j\sqrt{a_j}$ is nothing but $y_1\sqrt{a_1}$ + $y_2\sqrt{a_2}$ $-$ ln z. So, now you substitute all the values here, so because now everything is known, v is known, b is known, b$_1$ is known, a$_1$ is known, a$_2$ is known and then z also known, so everything is known, temperature is anyway given. So, simply if you substitute, you will get ln ϕ_1, that is $ln\frac{f_1}{y_1P}$ is nothing but 0.0553.

That means ϕ_1 = 1.057 and then f$_1$ = 21.03 bar, straightforward once you have these constants and then v$_{mixt}$ and z$_{mixt}$, simply substitution and getting them, right? Similarly, for the second component if you do $ln\frac{f_2}{y_2P}$ = ln $\left(\frac{v}{v-b}\right)$+ b$_i$, so now i = 2, so then it should be $\frac{b_2}{v-b} - 2\sqrt{a_i}$, i = 2, so $\frac{2\sqrt{a_2}}{vRT}$ and then $\sum y_j\sqrt{a_j}$ is nothing but $y_1\sqrt{a_1}$ + y$_2$ $\sqrt{a_2}$ because it is a binary mixture – ln z is as it is.

So, everything is known here also. If you substitute ln ϕ_2 you will get minus 0.2212. That means ϕ_2 = 0.8016 and then f$_1$ is nothing but 16.12 bar. So, we have 3 parts in the question. One is obviously f$_1$, another one is the obviously f$_2$, right? And then third one f$_{mixt}$ also we have to find out, f$_{mixt}$ we have already derived this expression in one of the previous lecture as a kind of example problem. So, ln f$_{mixt}$ is going to be y$_1$ $ln\frac{f_1}{y_1}$ + y$_2$ $ln\frac{f_2}{y_2}$, this also we have derived in one of the previous lecture.

So, now f$_1$, f$_2$, y$_1$, y$_2$ are known, you substitute here, so then you get ln f$_{mixt}$ is nothing but 3.60545. That means f$_{mixt}$ is nothing but 36.7982 bar, okay? That means ϕ_{mixt} is nothing but $\frac{f_{mixt}}{P}$, so that is 0.92. So, what you can see here? The non-ideality is very less for the mixture especially because you know ϕ value is 0.92 and then f$_{mixt}$ is not far away from the total pressure, total pressure is the 40 bar of the system, but now here f$_{mixt}$ is approximately 37 bar, 36.8, so that approximately 37 bar we can say.

So, the fugacity of the mixture is not far away from the total pressure, so then we can say the non-ideality in this particular system is very less, okay? This is how we can analyze from the result also, right?

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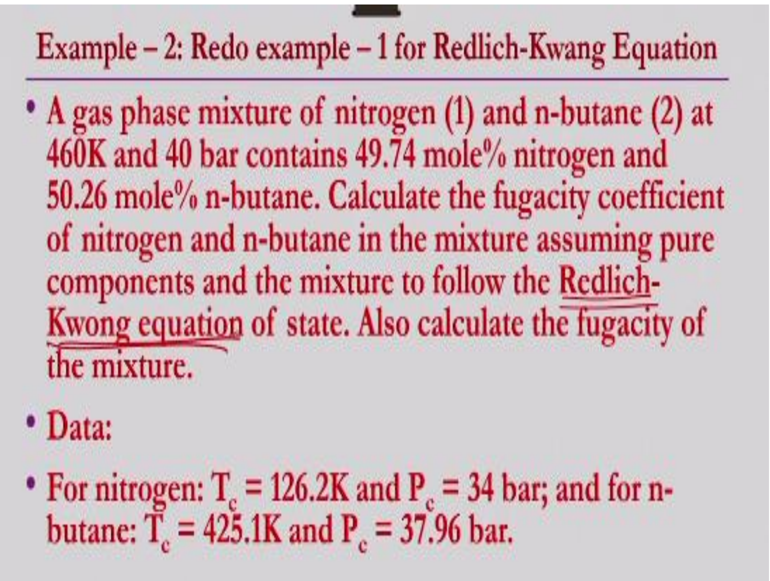

Example – 2: Redo example – 1 for Redlich-Kwang Equation

- A gas phase mixture of nitrogen (1) and n-butane (2) at 460K and 40 bar contains 49.74 mole% nitrogen and 50.26 mole% n-butane. Calculate the fugacity coefficient of nitrogen and n-butane in the mixture assuming pure components and the mixture to follow the Redlich-Kwong equation of state. Also calculate the fugacity of the mixture.
- Data:
- For nitrogen: T_c = 126.2K and P_c = 34 bar; and for n-butane: T_c = 425.1K and P_c = 37.96 bar.

Now, we take another example problem. What we are going to do? We are going to do the same problem example 1, but only change that we are going to make, we are making or we are taking that the individual components as well as the mixture of 2 components are obeying Redlich-Kwong equation, right? So, then what could be the answers, just wanted to check because for this system when we are using Van der Waal's equation of state we are finding that the non-ideality is very less.

Then we know Redlich-Kwong equation is improved, much is a kind of better equation of state compared to the Van der Waal's equation of state. So, can we have a kind of a much better reliability or much better understanding about the fugacity or non-ideality of the system by applying a better equation of state, for that purpose only we are doing the same problem with different equation of state, right?

So, composition and then data everything are going to be same because critical conditions are not going to change for any component by changing the equation of state but they are property of the system. So, everything is same except this Redlich-Kwong equation of state that we are going to use.

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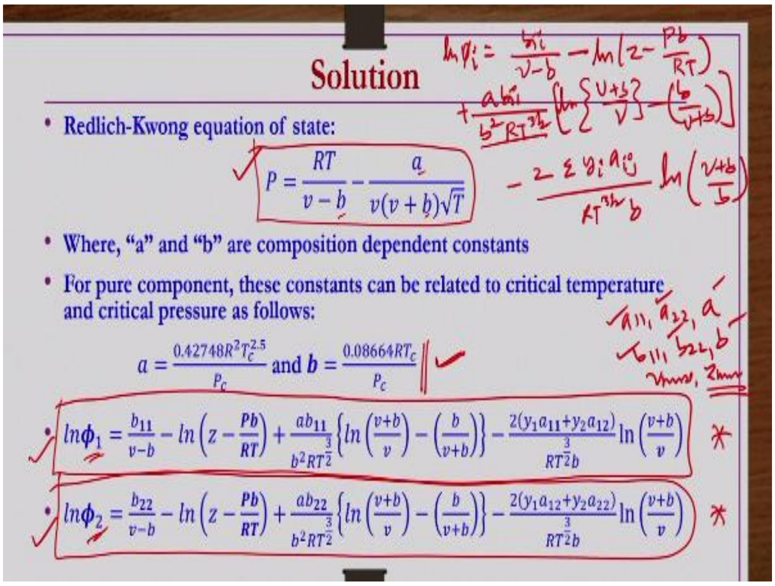

Solution

- Redlich-Kwong equation of state:

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

- Where, "a" and "b" are composition dependent constants
- For pure component, these constants can be related to critical temperature and critical pressure as follows:

$$a = \frac{0.42748R^2T_c^{2.5}}{P_c} \text{ and } \boldsymbol{b} = \frac{0.08664RT_c}{P_c}$$

- $$ln\phi_1 = \frac{b_{11}}{v-b} - ln\left(z - \frac{Pb}{RT}\right) + \frac{ab_{11}}{b^2RT^{\frac{3}{2}}}\left\{ln\left(\frac{v+b}{v}\right) - \left(\frac{b}{v+b}\right)\right\} - \frac{2(y_1a_{11}+y_2a_{12})}{RT^{\frac{3}{2}}b}\ln\left(\frac{v+b}{v}\right)$$ *
- $$ln\phi_2 = \frac{b_{22}}{v-b} - ln\left(z - \frac{Pb}{RT}\right) + \frac{ab_{22}}{b^2RT^{\frac{3}{2}}}\left\{ln\left(\frac{v+b}{v}\right) - \left(\frac{b}{v+b}\right)\right\} - \frac{2(y_1a_{12}+y_2a_{22})}{RT^{\frac{3}{2}}b}\ln\left(\frac{v+b}{v}\right)$$ *

$$\ln\phi_i = \frac{b_{ii}}{v-b} - \ln\left(z - \frac{Pb}{RT}\right) + \frac{a b_{ii}}{b^2 R T^{3/2}}\left[\ln\left\{\frac{v+b}{v}\right\} - \left(\frac{b}{v+b}\right)\right] - \frac{2\sum y_i a_{ij}}{RT^{3/2} b}\ln\left(\frac{v+b}{b}\right)$$

a_{11}, a_{22}, a

b_{11}, b_{22}, b

v_{mix}, z_{mix}

We know this Redlich-Kwong one equation as P $= \frac{\text{RT}}{v-b} - \frac{a}{v(v+b)\sqrt{T}}$, this we already know, right? Now here T is given, P is given, right? If you know a and b, then you can find out what is v, right? So, for that a and b for the mixture whatever are there that we have to find out in order to get the v_{mixt}, okay? This a and b we know that they are composition dependent constants, right? For pure component, these constants can be related to the critical temperature and pressure as a = $\frac{0.42748R^2T_c^{2.5}}{P_c}$ and b = $\frac{0.08664\,RT_c}{P_c}$.

These things are also we have already derived for Redlich-Kwong equations when we are discussing corresponding states theory, okay? So, now, if you apply the same mixing rule and then try to find out what is ln ϕ_1, ln ϕ_2, then you get this expression, this we have not derived actually. This we have not derived but it is not very difficult as I mentioned, we have this equation RT ln $\phi_i = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dV$ $-$ RT ln z and integration from v to infinity, right? This we know.

So, now from here this equation of state whatever it is there, you find out what is $\frac{\partial P}{\partial n_i}$ for ith component, general expression you can find out, then you can use it for the binary system. Then this $\frac{\partial P}{\partial n_i}$ you substitute here and then simplify the expression, then whatever this part is there you integrate and then what is z in terms of $\frac{Pv}{RT}$ etc., those things you find out, then you substitute this z also here, simplify, then you are going to get this expression.

For component 1, you are going to find out this expression, for component 2 you are going to find out this expression or you are going to find out ln ϕ_i for generalized one is nothing but $\frac{b_{ii}}{v-b} - ln\left(z - \frac{Pb}{RT}\right) + \frac{ab_{ii}}{b^2RT^{\frac{3}{2}}}\left\{ln\left(\frac{v+b}{v}\right) - \left(\frac{b}{v+b}\right)\right\}$. These two terms are being multiplied by this particular term and then last term is going to be $-\frac{2\sum y_i a_{jj}}{RT^{\frac{3}{2}}b} ln\left(\frac{v+b}{v}\right)$, where a and b without any subscript are for the mixtures, whereas the a and b with subscript ii or jj are for the component i and j, pure component i and pure component j.

So, this you can derive, you can do yourself and you get this thing. We are not going to derive this thing because we have done several such kind of things already. So, now if you wanted to find out ln ϕ_1, ϕ_2 what you need to find out? You need to find out a_{11}, a_{22}, then a_{mixt}, then b_{11}, b_{22}, then b_{mixt}, and then v_{mixt} and z_{mixt} you have to find out. a_{11}, a_{22}, b_{11}, b_{22}, you can find out by T_c, P_c information for pure component, a and b also you can find out by using mixing rules because y_1, y_2 are given.

So, once these things are known, v_{mixt} you can find out from the equation of state. Once v_{mixt} is known, then z_{mixt} can be known by $= \frac{Pv_{mixt}}{RT}$ because R, T, and P are known, v you just calculated, straightforward same as a previous problem that is what we are going to do now. Now unlike the previous problem, now I am using a_{11}, a_{22}, b_{11}, b_{22}, so that we can be comfortable with both kind of notations.

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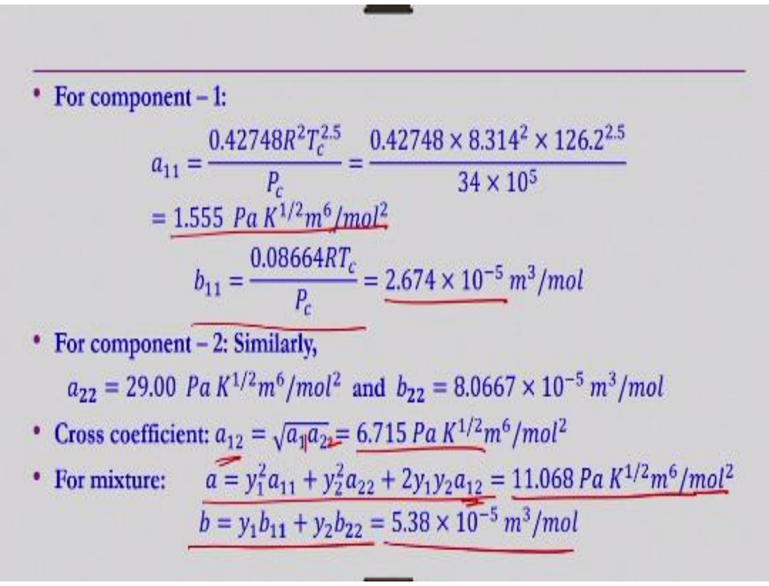

- For component – 1:

$$a_{11} = \frac{0.42748R^2T_c^{2.5}}{P_c} = \frac{0.42748 \times 8.314^2 \times 126.2^{2.5}}{34 \times 10^5}$$
$$= 1.555\ Pa\,K^{1/2}m^6/mol^2$$
$$b_{11} = \frac{0.08664RT_c}{P_c} = 2.674 \times 10^{-5}\ m^3/mol$$

- For component – 2: Similarly,

$a_{22} = 29.00\ Pa\,K^{1/2}m^6/mol^2$ and $b_{22} = 8.0667 \times 10^{-5}\ m^3/mol$

- Cross coefficient: $a_{12} = \sqrt{a_{11}a_{22}} = 6.715\ Pa\,K^{1/2}m^6/mol^2$
- For mixture: $a = y_1^2a_{11} + y_2^2a_{22} + 2y_1y_2a_{12} = 11.068\ Pa\,K^{1/2}m^6/mol^2$

$b = y_1b_{11} + y_2b_{22} = 5.38 \times 10^{-5}\ m^3/mol$

So, for the component 1, a_{11}, if you substitute T_c and P_c of component, you will get this value and then similarly b_{11} again if you substitute T_c and P_c values of component 1, you get this value for b_{11}. Similarly, for component 2, a_{22}, b_{22} we are getting these values. We need to know cross coefficient that is $\sqrt{a_{11}a_{22}}$, then we have this information because we know we need it a_{12} in mixing rule because a is nothing but y_1^2 a_{11} + y_2^2 a_{22}+ 2 y_1 y_2 $\sqrt{a_{11}a_{22}}$ or $\sqrt{a_{12}}$.

So, when you substitute everything because all these things are known including the y_1, y_2, then you will get a for the mixture as this number and then similarly $b = y_1 b_{11} + y_2 b_{22}$, then b you will get this number for the mixture, right?

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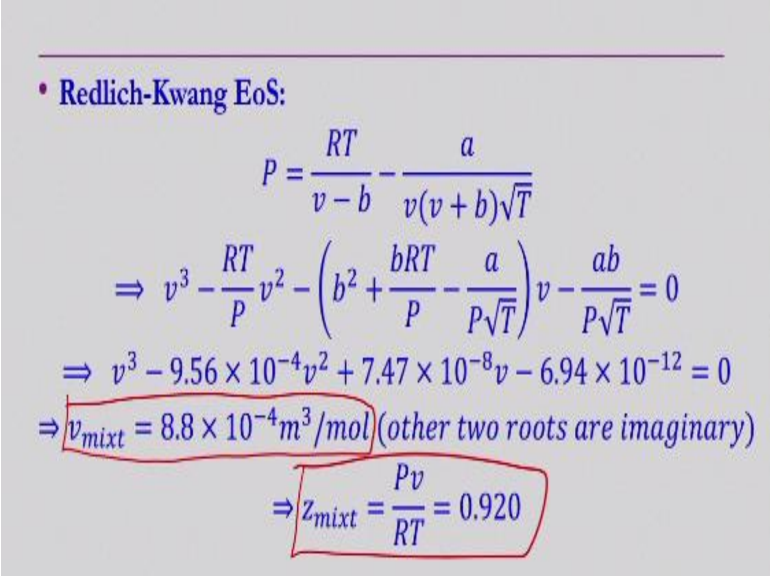

- **Redlich-Kwang EoS:**

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

$$\Rightarrow v^3 - \frac{RT}{P}v^2 - \left(b^2 + \frac{bRT}{P} - \frac{a}{P\sqrt{T}}\right)v - \frac{ab}{P\sqrt{T}} = 0$$

$$\Rightarrow v^3 - 9.56\times10^{-4}v^2 + 7.47\times10^{-8}v - 6.94\times10^{-12} = 0$$

$$\Rightarrow \boxed{v_{mixt} = 8.8\times10^{-4}m^3/mol}\,(other\ two\ roots\ are\ imaginary)$$

$$\Rightarrow \boxed{z_{mixt} = \frac{Pv}{RT} = 0.920}$$

So, once a and b are known, what you can do? You can expand the equation of state in a kind of cubic and molar volume expression because in this equation of state now except the molar volume everything is known including a and b, a and b we found, T and P are given. Then we solve this cubic equation, then you will be having 3 roots out of which only one is the real root that is $8.8*10^{-4}$ meter cube per mole. So v_{mixt} is also obtained. Once v_{mixt} is known, then z_{mixt} is straightforward that is $\frac{Pv_{mixt}}{RT}$ that we get 0.92, right?

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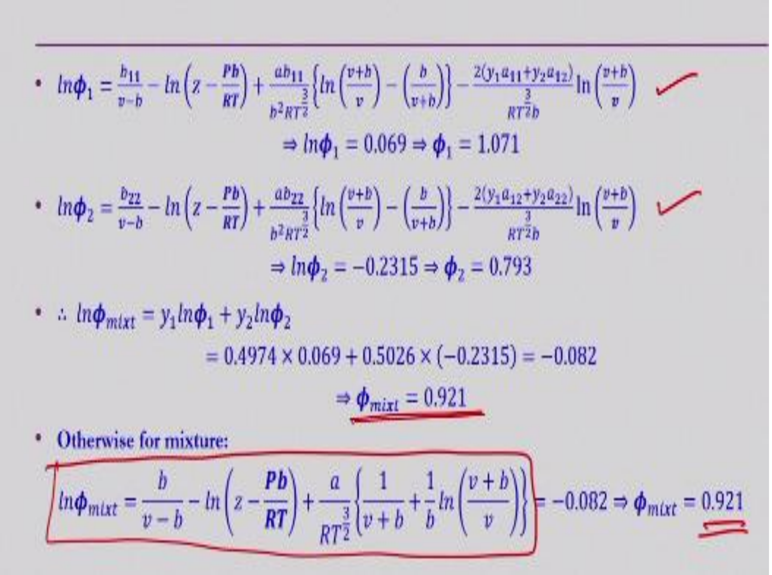

- $$ln\phi_1 = \frac{b_{11}}{v-b} - ln\left(z - \frac{Pb}{RT}\right) + \frac{ab_{11}}{b^2RT^{\frac{3}{2}}}\left\{ln\left(\frac{v+b}{v}\right) - \left(\frac{b}{v+b}\right)\right\} - \frac{2(y_1a_{11}+y_2a_{12})}{RT^{\frac{3}{2}}b}\ln\left(\frac{v+b}{v}\right)$$ ✓

$$\Rightarrow ln\phi_1 = 0.069 \Rightarrow \phi_1 = 1.071$$

- $$ln\phi_2 = \frac{b_{22}}{v-b} - ln\left(z - \frac{Pb}{RT}\right) + \frac{ab_{22}}{b^2RT^{\frac{3}{2}}}\left\{ln\left(\frac{v+b}{v}\right) - \left(\frac{b}{v+b}\right)\right\} - \frac{2(y_1a_{12}+y_2a_{22})}{RT^{\frac{3}{2}}b}\ln\left(\frac{v+b}{v}\right)$$ ✓

$$\Rightarrow ln\phi_2 = -0.2315 \Rightarrow \phi_2 = 0.793$$

- $$\therefore ln\phi_{mixt} = y_1ln\phi_1 + y_2ln\phi_2$$

$$= 0.4974 \times 0.069 + 0.5026 \times (-0.2315) = -0.082$$

$$\Rightarrow \underline{\phi_{mixt} = 0.921}$$

- **Otherwise for mixture:**

$$\boxed{ln\phi_{mixt} = \frac{b}{v-b} - ln\left(z - \frac{Pb}{RT}\right) + \frac{a}{RT^{\frac{3}{2}}}\left\{\frac{1}{v+b} + \frac{1}{b}ln\left(\frac{v+b}{v}\right)\right\}} = -0.082 \Rightarrow \phi_{mixt} = \underline{0.921}$$

So, now in ln ϕ_1, ln ϕ_2 expression everything is known except the f_1 value, so that you can obtain in the right hand side by substituting all these numbers, a_{11}, b_{11}, a, b, v, z, etc., whatever the required information you substitute in this expression in the right hand side, so that left hand side ln ϕ_1 you will get 0.069, that means $\phi_1 = 1.071$ and then ln ϕ_2 similarly if you substitute all these b_{22}, a_{22}, a_{11}, b_{11}, a, b, v, and z for the mixture in this right hand side of this expression, then you will get ln ϕ_2 as minus 0.2315.

That means, ϕ_2 is nothing but 0.793. Then, for the mixture, we know that ln ϕ_{mixt} is nothing but y_1 ln ϕ_1 + y_2 ln ϕ_2. That means you get ϕ_{mixt} is nothing but 0.921. That means, again we are getting the same value as we have considered the Van der Waal's equation, then whatever the ϕ_{mixt} there the same thing we are getting now also 0.921. In the previous problem also when we have taken Van der Waal's equation of state, then also ϕ_{mixt} we got it as 0.921.

So, that means, the system is not having much non-ideality. So, whether you use the Van der Waal's equation of state which is slightly less accurate compared to the Redlich-Kwong equation, you are going to get the same results, okay? Otherwise for the mixture also you can find out this expression for the ln ϕ_{mixt} the similar way. Then also you are going to get the 0.921 same expression for a fugacity coefficient of the mixture, right? This is how we can do the problems for the mixture of gases at higher densities.

So, in the next lecture, we are going to take much more complicated issues of fugacities in gaseous mixture, okay? When we have a kind of solubility of a liquid or a solid in compressed gases, those kind of thing we are going to discuss in the next lecture.

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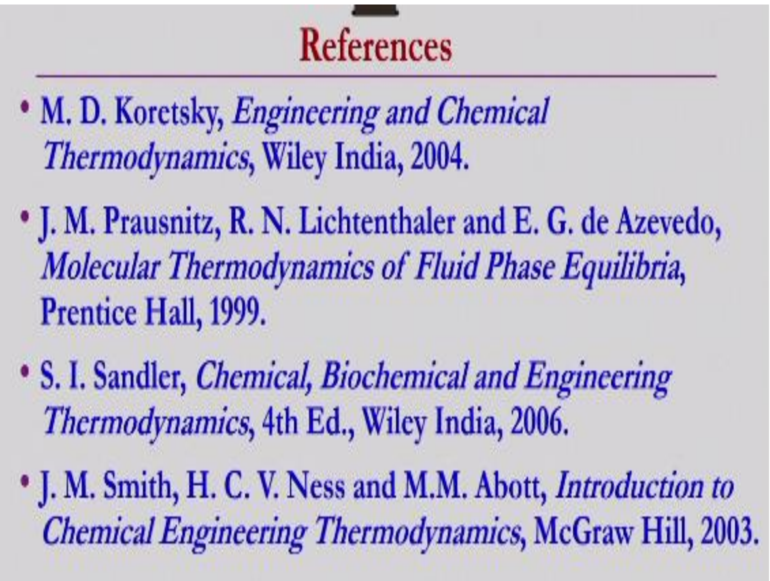

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So, the references for this particular lecture are nothing but Koretsky, Engineering and Chemical Thermodynamics; Prausnitz et al, Molecular Thermodynamics of Fluid Phase equilibria; Sandler, Chemical, Biochemical and Engineering thermodynamics; and Smith et al Introduction to Chemical Engineering Thermodynamics.

Thank you.