Advanced Thermodynamics
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Lecture – 14
Fugacities in Gaseous Mixtures

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is fugacities in gaseous mixture. So, till now what we have seen? We have seen most of the aspects related to the non-ideality of the system and then fugacity calculations for the different types of equations of state, those things we have seen. In other words, whatever the required things are there in order to calculate the fugacity of a real gaseous system, we have almost got all aspects related to that so that we can calculate the fugacities for a given problem, okay?

So, now what we do? We see a few example problems or real-life problems associated with the fugacity calculation, so from that fugacity calculations if we can provide some kind of information like precipitation, condensation, etc., occurring those kinds of processes. Now, we can apply these principles and then check how much information we can get applying the principles that we have studied, right? So, that is what we are going to see, but however, before that what we see? We have a kind of recapitulation what we have seen.

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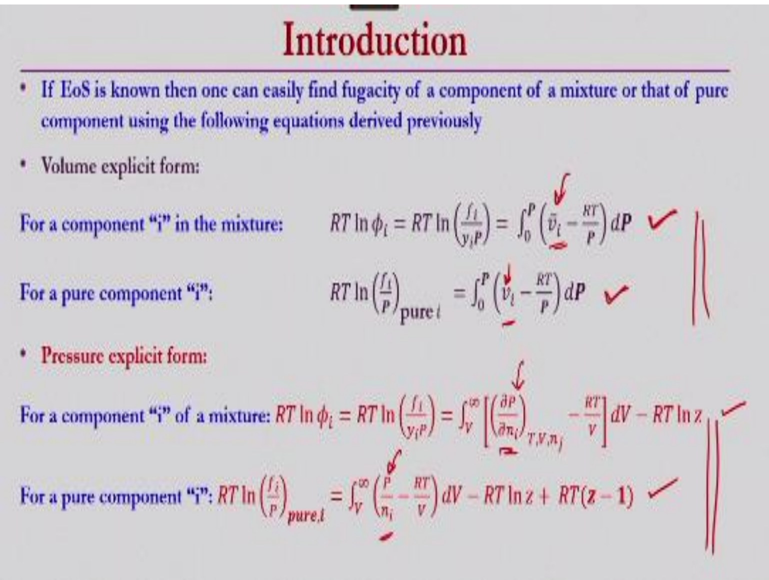

Introduction

- If EoS is known then one can easily find fugacity of a component of a mixture or that of pure component using the following equations derived previously
- Volume explicit form:

For a component "i" in the mixture: $RT\ln\phi_i = RT\ln\left(\frac{f_i}{y_iP}\right) = \int_0^P\left(\bar{v}_i - \frac{RT}{P}\right)dP$ ✓

For a pure component "i": $RT\ln\left(\frac{f_i}{P}\right)_{\text{pure } i} = \int_0^P\left(v_i - \frac{RT}{P}\right)dP$ ✓

- Pressure explicit form:

For a component "i" of a mixture: $RT\ln\phi_i = RT\ln\left(\frac{f_i}{y_iP}\right) = \int_V^\infty\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right]dV - RT\ln z$ ✓

For a pure component "i": $RT\ln\left(\frac{f_i}{P}\right)_{\text{pure},i} = \int_V^\infty\left(\frac{P}{n_i} - \frac{RT}{V}\right)dV - RT\ln z + RT(z-1)$ ✓

So, we have seen that if we know the equation of state, equation of state in different forms we know that pressure explicit form or volume explicit form then fugacity of component i in the mixture you can calculate using appropriate principles. Let us say if you have a volume explicit form equation of state, then this equation you can use in order to get the fugacity of component i in the mixture where the $\bar{v}_i$ is nothing but partial molar volume of that particular component in the mixture.

If you have a kind of component i as a kind of pure component, then you can use here this equation to get the fugacity of that particular component pure i and then here v_i is nothing but a molar volume of that particular component. If equation of state if you have in pressure explicit form that is pressure terms are in one side and all other rest of the terms other than the pressure are in the right hand side, then for a component i in the mixture, the fugacity you can calculate using this equation where here $\frac{\partial P}{\partial n_i}$ as per the equation of state we have to substitute and then simplify the equation.

If you have a pure component i, then this $\frac{P}{n_i}$ you have to substitute here and then integrate this equation and get the expressions. So, these are the generalized equation irrespective of what kind of equation of state we are using kind of thing right, okay? So, these are much generalized ones. Now depending on the equation of state, you can apply and then obtain a kind of fugacity expression generalized to each group of equation of state, okay? So, let us say for Van der Waal's equations are gases which obey Van der Waal's equation we have seen, what the expression for fugacity are.

Similarly, Redlich-Kwong equation we have seen, Peng-Robinson equation we have seen, and then we have also seen how to obtain the constants associated with this equation of state using the corresponding states theory, etc., those kinds of things we have seen, right? If it is virial equation of state, so the corresponding expressions you can substitute here or here and then get the required fugacity information.

So, for virial the equation of state also we have seen how to obtain the virial coefficients, etc., from the intermolecular potential as well as the corresponding states theory, those things we have seen. So, that means almost all information we have in order to find out the fugacity of the component i in a mixture or fugacity of pure component i as in a kind of pure form. So, those things we can do now. So, now we can apply these principles in real-life problems.

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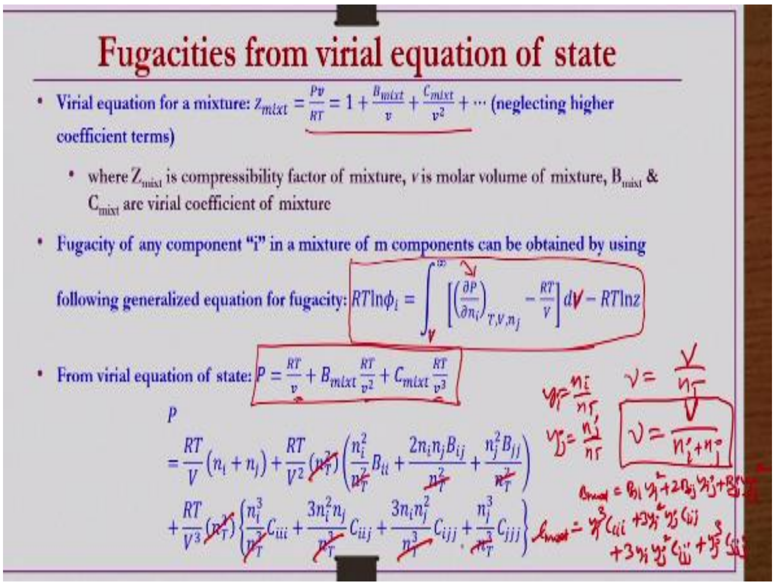

Fugacities from virial equation of state

- Virial equation for a mixture: $z_{mixt} = \frac{Pv}{RT} = 1 + \frac{B_{mixt}}{v} + \frac{C_{mixt}}{v^2} + \cdots$ (neglecting higher coefficient terms)
  - where Z_{mixt} is compressibility factor of mixture, v is molar volume of mixture, B_{mixt} & C_{mixt} are virial coefficient of mixture
- Fugacity of any component "i" in a mixture of m components can be obtained by using following generalized equation for fugacity: $\boxed{RT\ln\phi_i = \int_V^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right]dV - RT\ln z}$
- From virial equation of state: $\boxed{P = \frac{RT}{v} + B_{mixt}\frac{RT}{v^2} + C_{mixt}\frac{RT}{v^3}}$

$$P = \frac{RT}{V}(n_i + n_j) + \frac{RT}{V^2}(\cancel{n_T^2})\left(\frac{n_i^2}{\cancel{n_T^2}}B_{ii} + \frac{2n_i n_j B_{ij}}{\cancel{n_T^2}} + \frac{n_j^2 B_{jj}}{\cancel{n_T^2}}\right)$$
$$+ \frac{RT}{V^3}(\cancel{n_T^3})\left\{\frac{n_i^3}{\cancel{n_T^3}}C_{iii} + \frac{3n_i^2 n_j}{\cancel{n_T^3}}C_{iij} + \frac{3n_i n_j^2}{\cancel{n_T^3}}C_{ijj} + \frac{n_j^3}{\cancel{n_T^3}}C_{jjj}\right\}$$

$y_i = \frac{n_i}{n_T}$, $y_j = \frac{n_j}{n_T}$

$v = \frac{V}{n_T}$

$\boxed{v = \frac{V}{n_i + n_j}}$

$B_{mixt} = B_{ii} y_i^2 + 2B_{ij} y_i y_j + B_{jj} y_j^2$

$C_{mixt} = y_i^3 C_{iii} + 3y_i^2 y_j C_{iij} + 3y_i y_j^2 C_{ijj} + y_j^3 C_{jjj}$

Now, what we do? Before solving some real-life problems, we will be discussing how to obtain generalized expression for fugacities of a component i or j in a mixture if the mixture obeys virial equation of state, right? For the mixture if it obeys the virial equation of state, then we know in the virial equation of state is nothing but $z_{mixt} = \frac{Pv}{RT} = 1 + \frac{B_{mixt}}{v} + \frac{C_{mixt}}{v^2}$ and so on so. We are taking only second and third virial coefficient and then higher virial coefficients we are not taking for simplicity, okay?

One reason is the simplicity, another reason instead information on those higher virial coefficient from the experimental studies is almost negligible. For B, that is second virial coefficient, we have enough data for the majority of gases, C also we have a very few data for pure gases, for mixtures even less information is available. So that is the reason we are taking only up to C that is third virial coefficient. Now, here this equation, what we have to do?

We will be writing this equation in a pressure explicit form that is pressure we will be having one side and all other terms we will be writing other side and then this generalized expression for fugacity of component i whatever is there are 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. This expression we have already seen actually, right? So this expression now what we try to do? Here in place of $\frac{\partial P}{\partial n_i}$ according to the virial equation of state what is this $\frac{\partial P}{\partial n_i}$ we will be finding out and then substitute here, okay?

So, for the virial equation of state if you write only up to third virial coefficient and write in pressure explicit from like this, then we can write P = $\frac{RT}{v}$ + $B_{mixt}\frac{RT}{v^2}$ + $C_{mixt}\frac{RT}{v^3}$. Now, this expression here what we have to find out? We have to find out what is a molar volume. This molar volume we have to write in terms of total volume divided by n_T total number of moles. So for that, what we do initially now, we take for two component system $\frac{V}{n_i+n_j}$ as total number of moles because only binary mixture we are taking.

So this information we use here, then pressure can be written like this, okay? And then this is nothing but B_{mixt}, we have already seen that B_{mixt} = B_{ii} y_i^2 + 2 B_{ij} y_i y_j + B_{jj} y_j^2, this is what we know and then y_i we can write it as $\frac{n_i}{n_T}$ and then y_j also we can write $\frac{n_i}{n_T}$ like this we can write. So, then we have this expression. Similarly, C_{mixt} also we have mixing rule for virial equations that we have written like previously y_i^3 C_{iii} + 3 $y_i^2 y_j$ C_{iij} + 3 y_i y_j^2 C_{ijj} + $y_j^3 C_{jjj}$, this is also we have seen.

So, accordingly here also for y_i you write $\frac{n_i}{n_T}$ and for y_j also you write $\frac{n_i}{n_T}$, so then we have this expression. So, now this here this n_T^2, this n_T^2 and then this n_T^3we can cancel.

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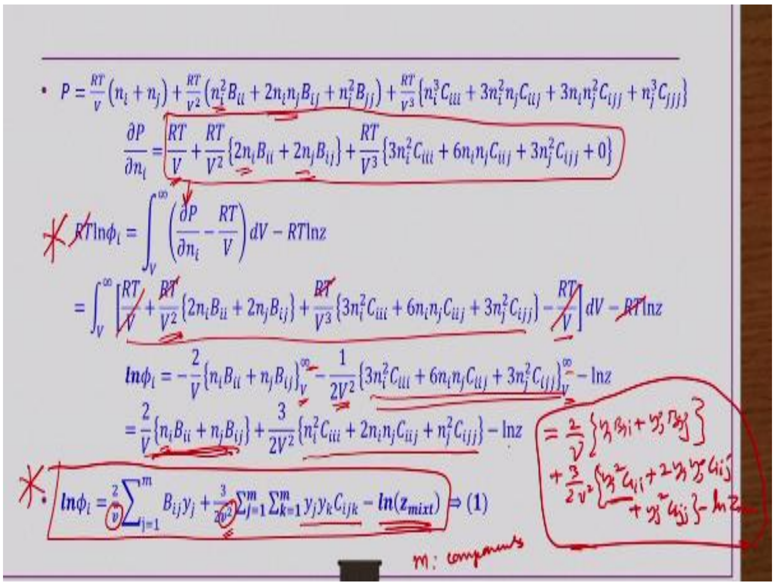

$$P = \frac{RT}{V}(n_i + n_j) + \frac{RT}{V^2}(n_i^2 B_{ii} + 2n_i n_j B_{ij} + n_j^2 B_{jj}) + \frac{RT}{V^3}\{n_i^3 C_{iii} + 3n_i^2 n_j C_{iij} + 3n_i n_j^2 C_{ijj} + n_j^3 C_{jjj}\}$$

$$\frac{\partial P}{\partial n_i} = \boxed{\frac{RT}{V} + \frac{RT}{V^2}\{2n_i B_{ii} + 2n_j B_{ij}\} + \frac{RT}{V^3}\{3n_i^2 C_{iii} + 6n_i n_j C_{iij} + 3n_j^2 C_{ijj} + 0\}}$$

$$* \; \cancel{RT}\ln\phi_i = \int_V^\infty \left(\frac{\partial P}{\partial n_i} - \frac{RT}{V}\right) dV - RT\ln z$$

$$= \int_V^\infty \left[\cancel{\frac{RT}{V}} + \frac{\cancel{RT}}{V^2}\{2n_i B_{ii} + 2n_j B_{ij}\} + \frac{\cancel{RT}}{V^3}\{3n_i^2 C_{iii} + 6n_i n_j C_{iij} + 3n_j^2 C_{ijj}\} - \cancel{\frac{RT}{V}}\right] dV - \cancel{RT}\ln z$$

$$\ln\phi_i = -\frac{2}{V}\{n_i B_{ii} + n_j B_{ij}\}_V^\infty - \frac{1}{2V^2}\{3n_i^2 C_{iii} + 6n_i n_j C_{iij} + 3n_j^2 C_{ijj}\}_V^\infty - \ln z$$

$$= \frac{2}{V}\{n_i B_{ii} + n_j B_{ij}\} + \frac{3}{2V^2}\{n_i^2 C_{iii} + 2n_i n_j C_{iij} + n_j^2 C_{ijj}\} - \ln z$$

$$\boxed{= \frac{2}{V}\{y_i B_{ii} + y_j B_{ij}\} + \frac{3}{2V^2}\{y_i^2 C_{iii} + 2y_i y_j C_{iij} + y_j^2 C_{ijj}\} - \ln z}$$

$$* \; \boxed{\ln\phi_i = \frac{2}{V}\sum_{j=1}^{m} B_{ij} y_j + \frac{3}{2V^2}\sum_{j=1}^{m}\sum_{k=1}^{m} y_j y_k C_{ijk} - \ln(z_{mixt})} \Rightarrow (1)$$

m: components

Then, we have this expression P = $\frac{RT}{V}\left(n_i + n_j\right) + \frac{RT}{V^2}$ and then all this expression is there. Now, if you partially differentiate this P with respect to n_i because for ith component we are doing. So, when you take with respect to n_i, n_j is constant, so $\frac{\partial P}{\partial n_i}$ = $\frac{RT}{V}$ (1 + 0) so that is $\frac{RT}{V}$and this is

$\frac{RT}{V^2}$ and differentiation of n_i^2 with respect to n_i is 2 n_i, here differentiation of $2n_in_j$ with respect to n_i is nothing but 2j and differentiation of n_j with respect to n_i is 0, so then third term is not there.

So, likewise differentiation of all other terms we are doing here, this third term in the RHS as well. Then we have this one. So, now this $\frac{\partial P}{\partial n_i}$ information whatever we got here for virial equation of state that we are substituting here in the generalized expression. This is the generalized expression irrespective of which equation of state it is. From here onwards depending on that equation of state, expression will change, okay? So, for this virial equation of state, $\frac{\partial P}{\partial n_i}$we have found it like this.

This is $\frac{\partial P}{\partial n_i}$, - $\frac{RT}{V}$is there, so $\frac{RT}{V}$ $\frac{RT}{V}$cancel out dV - RT ln z, right? So then this RT also if you cancel out from either side, so this RT is gone, this RT and this RT with the RT in the left hand side if we cancel out, so ln ϕ_i in the left hand side. The integration of this particular $\frac{1}{V^2} - \frac{1}{V}$. So, $-\frac{1}{V}$ (2 n_i B_{ii} + 2n_j B_{ij}) is there, 2 also we are taking as a common, same is integration of $\frac{1}{V^3}$ is $-\frac{1}{2V^2}$ will be having and then remaining terms would be constant, right?

So, then here next step what we are doing, we are taking we are substituting this V to infinity limits in either of the terms and then we are also taking 3 common from this second term of the RHS, so that we have $\frac{2}{V}$ (n_i B_{ii} + n_j B_{ij}) + $\frac{3}{2V^2}$ (n_i^2 C_{iii} + 2 n_i n_j C_{iij} + n_j^2 C_{ijj}) $-$ ln z is as it is, we are not doing anything with that one. So, if you generalize this one ln ϕ_i for multi-component system what do you get? Generalization as well as writing in terms of the molar volume, so now what we do?

Before generalization, you can see here, we are writing in terms of molar volume, that is coming because whatever n_i is there that in order to get the n_i as a kind of y_i terms what we are doing? First term in the RHS here, we are multiplying and dividing by n_T. So, $\frac{n_i}{n_T}$ = y_j and $\frac{n_T}{V} = \frac{1}{v}$, this is what we get. So, $\frac{2}{v}$we are getting here. Similarly, here also what we are doing, we are multiplying and dividing by n_T^2, so that $\frac{n_i^2}{n_T^2} = y_i^2$.

Then $\frac{n_i n_j}{n_T^2}$ is nothing but y_i y_j we get and then $\frac{n_T^2}{V^2}$ is nothing but $\frac{1}{v^2}$, so that this is what we have here $\frac{2}{v}$(y_i B_{ii} + y_j B_{ij}) + $\frac{3}{2v^2}$ $y_i^2$$C_{iii}$ + 2 y_i y_j C_{iij} + y_j^2 C_{ijj} - ln z_{mixt}, this is what we have. So, this is for the binary system. If you write it for a multi-component system, so the first term would become $\frac{2}{v}$ as it is, this would be $\sum B_{ij} y_{jj}$ is changing from 1 to m for m number of components are there, right?

Similarly, here second term $\frac{3}{2v^2}$ would be as it is and then $\sum_{j=1}^{m} \sum_{k=1}^{m} y_i y_j C_{ijk} -$ ln z_{mixt}. Let us say if j = i and then k = i, then what should be this first term, it should be y_i * y_i that is $y_i^2$and then C_{iii} that is C_{iii}, so that is the first time here like this, okay? So, like that you know we can generalize and then third term - ln z_{mixt}. So, this is for m number of components that are present in the system and then whereas this one is for the binary system having 2 components i and j, right?

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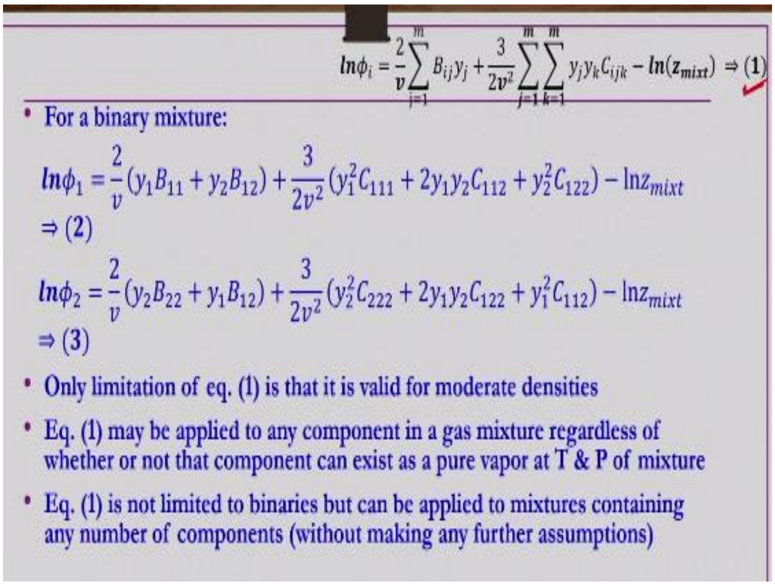

$$ln\phi_i = \frac{2}{v}\sum_{j=1}^{m} B_{ij}y_j + \frac{3}{2v^2}\sum_{j=1}^{m}\sum_{k=1}^{m} y_j y_k C_{ijk} - ln(z_{mixt}) \Rightarrow (1)$$

- For a binary mixture:

$$ln\phi_1 = \frac{2}{v}(y_1B_{11} + y_2B_{12}) + \frac{3}{2v^2}(y_1^2C_{111} + 2y_1y_2C_{112} + y_2^2C_{122}) - \ln z_{mixt} \Rightarrow (2)$$

$$ln\phi_2 = \frac{2}{v}(y_2B_{22} + y_1B_{12}) + \frac{3}{2v^2}(y_2^2C_{222} + 2y_1y_2C_{122} + y_1^2C_{112}) - \ln z_{mixt} \Rightarrow (3)$$

- Only limitation of eq. (1) is that it is valid for moderate densities
- Eq. (1) may be applied to any component in a gas mixture regardless of whether or not that component can exist as a pure vapor at T & P of mixture
- Eq. (1) is not limited to binaries but can be applied to mixtures containing any number of components (without making any further assumptions)

So, this equation I have written here again for the requirement because now this equation we expand for 2 components, binary mixture i and j are 1 and 2. Then for component 1, we can write this equation ln ϕ_1 = $\frac{2}{v}$(y_1 B_{11} + y_2 B_{12}) + $\frac{3}{2v^2}$ y_1^2 C_{111} + 2 y_1 y_2 C_{112} + y_2^2 C_{122} - ln z_{mixt} we get. Similarly ln ϕ_2 we get this expression, right? So, this equation what is the limitation, it is valid for moderate densities only.

Because we know that virial equation our state is valid for the low to moderate densities only, though at high densities we can apply but it gives some kind of errors because of non-availability of this virial coefficient at high densities, okay? This equation 1 may also be applied to any number of component not necessarily for the binary without making any assumptions about the mixing rule that we have seen. So, we do not need any mixing rule here, okay?

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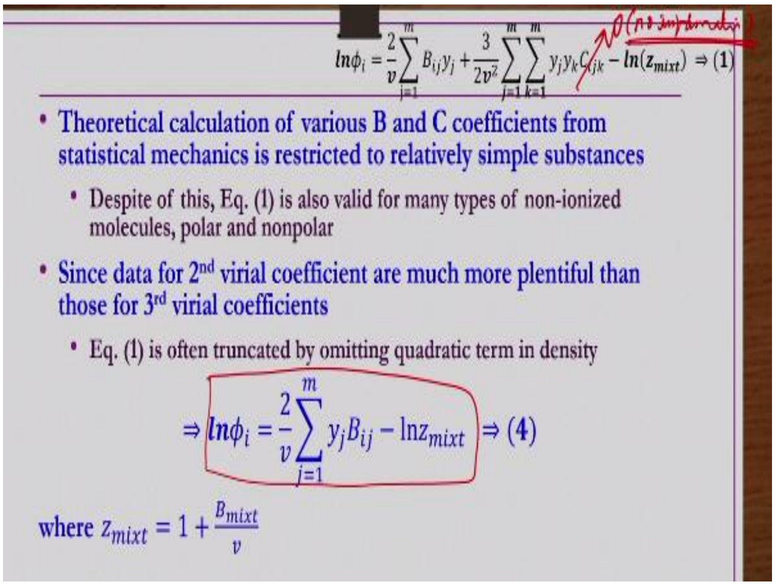

$$ln\phi_i = \frac{2}{v}\sum_{j=1}^{m} B_{ij}y_j + \frac{3}{2v^2}\sum_{j=1}^{m}\sum_{k=1}^{m} y_jy_k\cancel{C}_{ijk} - ln(z_{mixt}) \Rightarrow (1)$$

0 ([illegible])

- Theoretical calculation of various B and C coefficients from statistical mechanics is restricted to relatively simple substances
  - Despite of this, Eq. (1) is also valid for many types of non-ionized molecules, polar and nonpolar
- Since data for 2nd virial coefficient are much more plentiful than those for 3rd virial coefficients
  - Eq. (1) is often truncated by omitting quadratic term in density

$$\Rightarrow \boxed{ln\phi_i = \frac{2}{v}\sum_{j=1}^{m} y_jB_{ij} - \ln z_{mixt}} \Rightarrow (4)$$

where $z_{mixt} = 1 + \frac{B_{mixt}}{v}$

Further theoretical calculation of various B and C coefficient from statistical mechanics is restricted to relatively simple substances that we already know, right? Plenty of information is available for this B and C for simple molecules but for complicated molecules there is some information very little literature is available, right? So, despite of that one this equation number 1 is also valid for non-ionized molecules, polar, non-polar kind of complex molecules for all those things it is applicable, okay?

But only limitation is though it is applicable for other kind of molecules also that the limitations may be you may be finding difficulty in using this equation only in terms of what is corresponding B and C second and virial coefficient for those molecules that limitations you may be having, but equation point of view it is valid for complex molecules as well. Further data for second viral coefficient B sufficient data is available, but whereas for the third virial coefficient very small data is available and further higher virial coefficients data is very negligible, right?

So, considering this reason that for C data is very small, if you take this equation only up to second video coefficient, then what we have, we can get this expression ln ϕ = $\frac{2}{v}\sum B_{ij}y_i$ −ln z$_{mixt}$, because information about the third virial coefficient is very less, so we are not taking, it is not 0, no information or little information, very small information is available. In such conditions if you truncate or if you do not take the third virial coefficient in virial equation of state, then you get this expression, okay?

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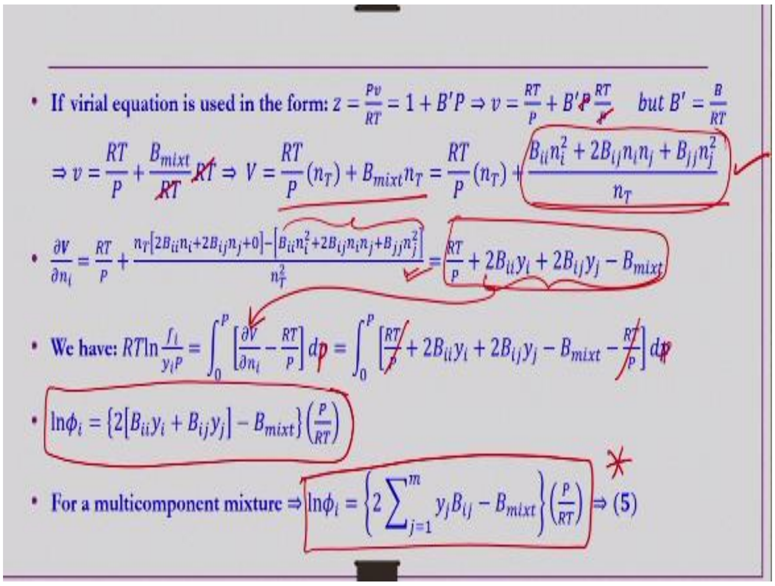

- If virial equation is used in the form: $z = \frac{Pv}{RT} = 1 + B'P \Rightarrow v = \frac{RT}{P} + B'\cancel{P}\frac{RT}{\cancel{P}}$ but $B' = \frac{B}{RT}$

$$\Rightarrow v = \frac{RT}{P} + \frac{B_{mixt}}{\cancel{RT}}\cancel{RT} \Rightarrow V = \underline{\frac{RT}{P}(n_T) + B_{mixt}n_T} = \frac{RT}{P}(n_T) + \boxed{\frac{B_{ii}n_i^2 + 2B_{ij}n_in_j + B_{jj}n_j^2}{n_T}}$$

- $\frac{\partial V}{\partial n_i} = \frac{RT}{P} + \frac{n_T[2B_{ii}n_i + 2B_{ij}n_j + 0] - \overbrace{[B_{ii}n_i^2 + 2B_{ij}n_in_j + B_{jj}n_j^2]}}{n_T^2} = \boxed{\frac{RT}{P} + \underbrace{2B_{ii}y_i + 2B_{ij}y_j - B_{mixt}}}$

- We have: $RT\ln\frac{f_i}{y_iP} = \int_0^P \left[\frac{\partial V}{\partial n_i} - \frac{RT}{P}\right]dp = \int_0^P \left[\cancel{\frac{RT}{P}} + 2B_{ii}y_i + 2B_{ij}y_j - B_{mixt} - \cancel{\frac{RT}{P}}\right]dp$

- $\boxed{\ln\phi_i = \{2[B_{ii}y_i + B_{ij}y_j] - B_{mixt}\}\left(\frac{P}{RT}\right)}$

- For a multicomponent mixture $\Rightarrow \boxed{\ln\phi_i = \left\{2\sum_{j=1}^{m} y_jB_{ij} - B_{mixt}\right\}\left(\frac{P}{RT}\right)} \Rightarrow (5)$ *

We have this z = $\frac{Pv}{RT}$ = 1 + B'P. So, this equation we can write v = $\frac{RT}{P}$ + B' P $\frac{RT}{P}$, so this is cancelled out, right? So, but B' we know it is nothing but $\frac{B}{RT}$. So, then we can write this expression as v = $\frac{RT}{P}$+ B$_{mixt}$. So, now v we can write it as $\frac{V}{n_T}$, v is molar volume, V is the total volume. So, n$_T$ if you take to the right hand side, so then we have $\frac{RT}{P}$(n$_T$)+ B$_{mixt}$ n$_T$, right? B$_{mixt}$ we know that this is B$_{ii}$ y_i^2 + 2 B$_{ij}$ y$_i$ y$_j$ + B$_{jj}$ y_j^2, that is what we are having.

So then y is if you write $\frac{n}{n_T}$then you can have this expression for the B$_{mixt}$, Then we need $\frac{\partial V}{\partial n_i}$ in order to substitute in the expression RT ln ϕ$_i$ = $\int_0^P$ v̄i − $\frac{RT}{P}dP$, right? That is the generalized expression. So there we need the v̄$_i$, v̄$_i$ is nothing but $\frac{\partial V}{\partial n_i}$. So if you do that once you have this expression, okay? $\frac{RT}{P}$ + this expression whatever this particular term, if you do the differentiation with respect to n$_i$, you will have this expression, right?

Further if you simplify this term will become 2 B$_{ii}$ y$_i$ + 2 B$_{ij}$ y$_j$ - B$_{mixt}$. So, this particular part entire thing is nothing but we can write it as B$_{mixt}$, this particular part divided by n_T^2 we can write it as a mixture, okay? So, now if you substitute this $\frac{\partial V}{\partial n_i}$ whatever this expression that we are having, right? Here, then you integrate it. This $\frac{RT}{P}$this $\frac{RT}{P}$is cancelled out. Then we have ln ϕ_i = 2 B_{ii} y_i + B_{ij} y_j - B_{mixt} $\frac{P}{RT}$, this is what we are getting, okay?

So, for binary mixture this is what we have i and j component that is we have taken, but if you have a multi-component system, multi-component system if we are having, then we can generalize this expression as ln ϕ_i = $\left\{2\sum_{j=1}^{m} y_i B_{ij} - B_{mixt}\right\}\left(\frac{P}{RT}\right)$. This is what we are having, okay? So, whether you write volume explicit form or pressure explicit form for this virial equation of state, so then we have a corresponding fugacity expression now for this equation of state as well. So, now we can go to solve a few example problems.

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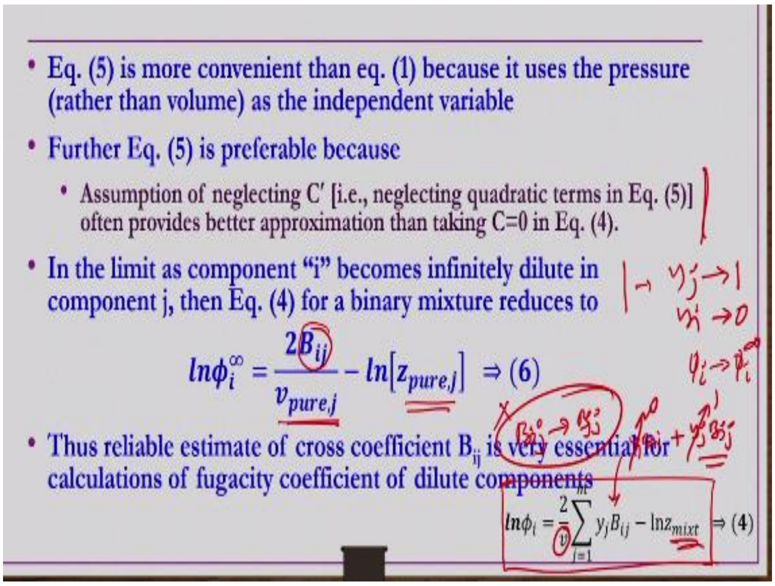

- Eq. (5) is more convenient than eq. (1) because it uses the pressure (rather than volume) as the independent variable
- Further Eq. (5) is preferable because
  - Assumption of neglecting C′ [i.e., neglecting quadratic terms in Eq. (5)] often provides better approximation than taking C=0 in Eq. (4).
- In the limit as component "i" becomes infinitely dilute in component j, then Eq. (4) for a binary mixture reduces to

$$ln\phi_i^{\infty} = \frac{2B_{ij}}{v_{pure,j}} - ln\left[z_{pure,j}\right] \Rightarrow (6)$$

- Thus reliable estimate of cross coefficient B_{ij} is very essential for calculations of fugacity coefficient of dilute components

$$ln\phi_i = \frac{2}{v}\sum_{j=1}^{m} y_j B_{ij} - \ln z_{mixt} \Rightarrow (4)$$

$y_j \to 1$
$y_i \to 0$
$\phi_i \to \phi_i^{\infty}$

Now, whatever the just obtained expression equation 5 in terms of, ln ϕ_i when you write as volume explicit form, then we find this equation it is more convenient to use why because in this equation, we have pressure as independent variable, which is much convenient to use in general, right? For any equation of state. Further also it is preferable, because in the virial equations, C' if you neglect, then it provides better approximation to the fugacities rather than neglecting C = 0 in virial coefficient, right? Because that is inducing more error that is what it has been found by the experimental observation, right?

C' you can neglect by neglecting C', C' neglecting in the sense you are writing z = 1 + B' P + C'P^2 and all that P series we have written, so there it is inducing less error if you remove or neglect the C', but in the form $z = 1 + \frac{B}{v} + \frac{C}{v^2}$ in that form, the C if you remove so that may induce large error in the subsequent calculations. So, that is the reason also the equation number 5 that we just derived that is better to use as well as the reliability is better.

Further in the limit as component i becomes infinitely dilute in component j, then what will happen to equation number 4 that we will see now, right? That equation number 4 is for the binary system. For the binary system, we have written this equation number 4, okay? $\frac{2}{v}\sum_{j=1}^{m} y_j B_{ij} - lnz_{mixt}$ we have taken for previous case. Now, the component i becomes infinitely dilute in component j that means $y_j \rightarrow 1$ and then $y_i \rightarrow 0$, so then $\phi_i \rightarrow \phi_a^{\infty}$, okay?

So that means, i component is very small. Then ln ϕ_i we get here in this equation, this is nothing but what we have y_1, let us say for the i^{th} component this should be y_i B_{ii} + y_j B_{ij}. So, now what happens? This $y_j = 1$, but $y_i = 0$, so what you have, y_j B_{ij} you are having, only that much you are having and then this $y_j \rightarrow 1$. So, that means y_j B_{ij} is nothing but B_{ij} or close to B_{ij} and then this since j is a lot or you know large amount close tending to 1, so what we can say, v_{mixt} is also equals to molar volume of (pure j), okay?

Similarly z_{mixt} also close to the $z_{pure\ j}$, okay? So, now, what happens in such kind of system let us say i becomes infinitely diluted in component j, that means you can say that is almost it is like a pure j component, then in general people may think that the whatever the result is like parameters associated to those pure j are also valid for the mixture, that is let us say whatever B_{ij} it is across virial coefficient, right? So, but when you say that j is large, almost pure j is there though it is a mixture of i and j, i is very small, j is very large.

So then you may be thinking that the B_{ij} may be close to the B_{jj}, but that is not in general, right? So we can see here so in that ln ϕ expression B_{ij} is there, it is very much important. So, if you wanted to obtain the fugacity coefficient of i, though it is present in very small amount, very small amount you need to have a kind of very accurate reliable information about this cross virial coefficient B_{ij}, you cannot take simply B_{ij} is close to B_{jj}, indeed we are going to see one example and then we realize that B_{ij} is very much far away or different from the B_{ii}, B_{jj}, right?

So, repeating that even the system is very dilute system, i is very small, negligible amount is there, j is very large amount is there, under such mixtures also, this cross virial coefficient B_{ij}

is going to be very much important one and then this B_{ij} you cannot approximate as close to or almost equals to B_{jj} considering that it is almost a pure j, though it is almost pure j, you cannot say that B_{ij} is approximately equals to B_{jj} that we demonstrate now using an example problem.

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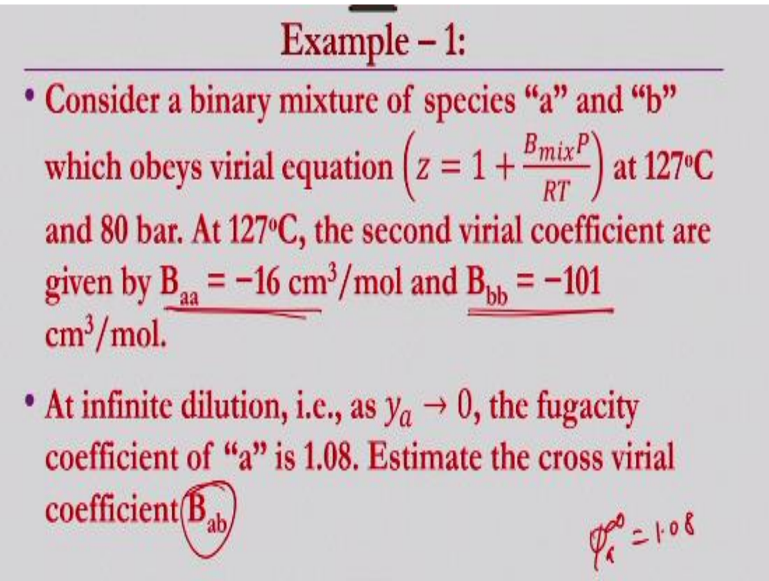

Example – 1:

- Consider a binary mixture of species "a" and "b" which obeys virial equation $\left(z = 1 + \frac{B_{mix}P}{RT}\right)$ at 127°C and 80 bar. At 127°C, the second virial coefficient are given by $\underline{B_{aa} = -16}$ $\underline{cm^3/mol}$ and $\underline{B_{bb} = -101}$ cm^3/mol.
- At infinite dilution, i.e., as $y_a \to 0$, the fugacity coefficient of "a" is 1.08. Estimate the cross virial coefficient B_{ab}

$\phi_a^\infty = 1.08$

So, consider a binary mixture of species a and b which obeys virial equation of state at 127 degrees centigrade and 80 bar. At this temperature, second virial coefficients of pure component are given B_{aa} and B_{bb} are given. B_{aa} is nothing but the pure second virial coefficient for pure a, B_{bb} is nothing but the second virial coefficient for pure b component, okay? At infinite dilution that is as $y_a \to 0$, the fugacity coefficient of a that is ϕ_a^∞ is given as 1.08.

Then estimate what is the cross virial coefficient B_{ab} that is B_{ab} is nothing but cross virial coefficient for the mixture, it is not for the B_{mixt}, it is the cross virial coefficient required to obtain the B_{mixt}.

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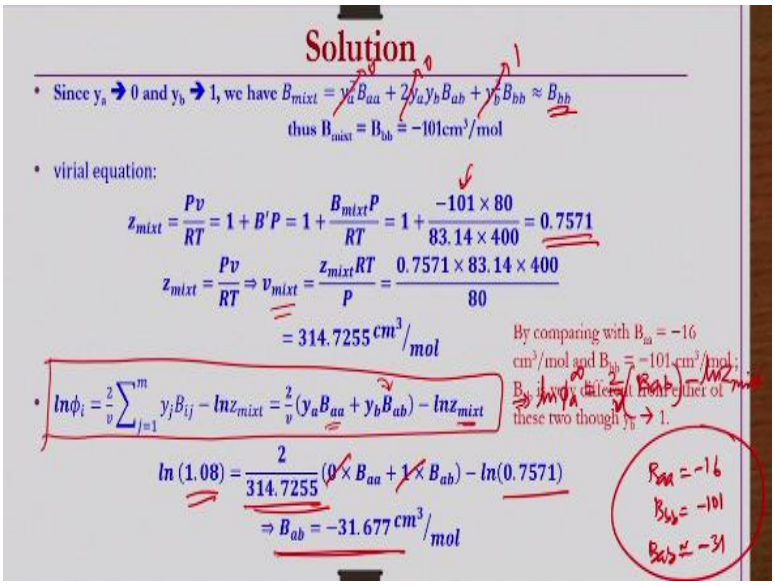

Solution

- Since $y_a \rightarrow 0$ and $y_b \rightarrow 1$, we have $B_{mixt} = \cancel{y_a^2}^{0} B_{aa} + 2\cancel{y_a}^{0} y_b B_{ab} + \cancel{y_b^2}^{1} B_{bb} \approx B_{bb}$

  thus $B_{mixt} = B_{bb} = -101 cm^3/mol$

- virial equation:

$$z_{mixt} = \frac{Pv}{RT} = 1 + B'P = 1 + \frac{B_{mixt}P}{RT} = 1 + \frac{-101 \times 80}{83.14 \times 400} = 0.7571$$

$$z_{mixt} = \frac{Pv}{RT} \Rightarrow v_{mixt} = \frac{z_{mixt}RT}{P} = \frac{0.7571 \times 83.14 \times 400}{80}$$

$$= 314.7255\, {cm^3}/{mol}$$

- $$\boxed{ln\phi_i = \frac{2}{v}\sum_{j=1}^{m} y_j B_{ij} - lnz_{mixt} = \frac{2}{v}(y_a B_{aa} + y_b B_{ab}) - lnz_{mixt}}$$

$$ln\,(1.08) = \frac{2}{314.7255}(\cancel{0} \times B_{aa} + \cancel{1} \times B_{ab}) - ln(0.7571)$$

$$\Rightarrow B_{ab} = -31.677\, {cm^3}/{mol}$$

By comparing with $B_{aa} = -16$ cm^3/mol and $B_{bb} = -101$ cm^3/mol; B_{ab} is very different from either of these two though $y_b \rightarrow 1$.

$\Rightarrow ln\phi_a^\infty = \frac{2}{v}(B_{ab}) - lnz_{mixt}$

$B_{aa} = -16$
$B_{bb} = -101$
$B_{ab} \simeq -31$

Since $y_a \rightarrow 0$, $y_b \rightarrow 1$ here, so then $B_{mixt} = y_a^2 B_{aa} + 2y_a y_b B_{ab} + y_b^2 B_{bb}$ is there. So, this we can write approximately B_{bb} because y_b is close to 1 and then $y_a = 0$. So, first two terms are almost 0. So, we can write approximately $B_{mixt} = B_{bb}$, right? So, then we need a z_{mixt}, we need z_{mixt} because that equation we are going to use to get the cross virial coefficient is having z_{mixt} term. So the z_{mixt} is nothing but it is given as $1 + B_{mixt} \frac{P}{RT}$.

So, B_{mixt} is now you obtained as approximated as 101 because it is a kind of pure this thing, then you have a $z_{mixt} = 0.7571$, right? And then if you have z_{mixt}, you can find it out v_{mixt} as $z_{mixt} \frac{RT}{P}$. When you do this one, you get v_{mixt} as 314.7255 centimeter cube per mole. Actually up to this part, we have already seen in one of the lecture finding out only z_{mixt} and v_{mixt}, right?

Now, next level to this one, if you wanted to obtain the cross virial coefficient, so you have to use this expression because now here z_{mixt} is known, y_a and y_b are given, y_a is close to 0, y_b is close to 1, B_{aa} are given and then this one you have to find out, B_{ab} you have to find out, even this ln ϕ_a^∞ is also given. So, now from here this expression for this problem what we get, we can have ln ϕ_a^∞ = 2 by v, y_a is almost 0 so we are not taking, y_b is almost 1 so you can take it as a kind of 1 and then B_{ab} - ln z_{mixt}, right?

So, now ln ϕ_a^∞ is given as 1.08, 2 by v obtained this one, y_a is 0, y_b is 1, and then z_{mixt} you got 0.7571. So, then here, B_{ab} you can see it is - 31.677 centimeter cube per mole. Now, it is very different from B_{aa} or B_{bb} because this B_{aa} it is given as - 16, B_{bb} is given as - 101 centimeter cube per mole and then B_{ab} we got it as - 31 roughly approximately. So, how much different it is from B_{bb} or the second virial coefficient of pure b is far away, I mean very different, right?

So, the cross virial coefficient we cannot take based on the consideration whether it is a dilute system or not, we have to follow the principles whatever available, okay?

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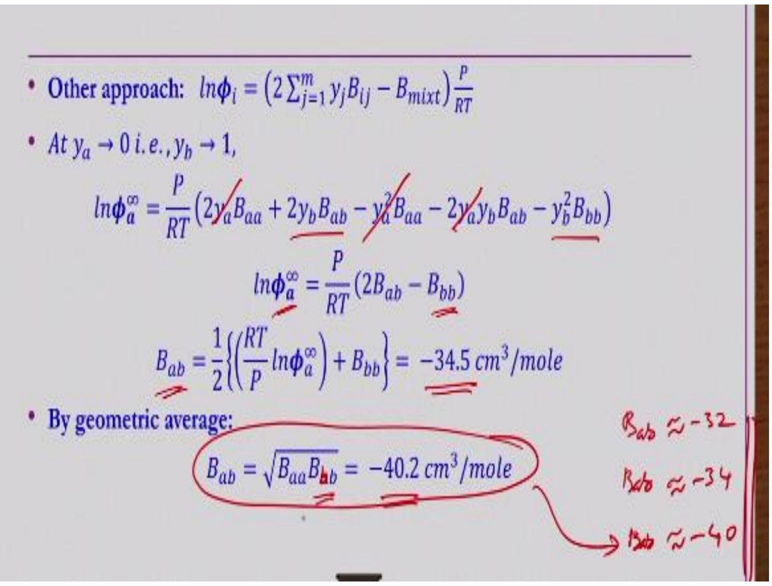

- Other approach: $ln\phi_i = \left(2\sum_{j=1}^{m} y_j B_{ij} - B_{mixt}\right)\frac{P}{RT}$
- At $y_a \to 0$ i.e., $y_b \to 1$,

$$ln\phi_a^{\infty} = \frac{P}{RT}\left(2\cancel{y_a}B_{aa} + \underline{2y_bB_{ab}} - \cancel{y_a^2}B_{aa} - 2\cancel{y_a}y_bB_{ab} - \underline{y_b^2B_{bb}}\right)$$

$$ln\phi_a^{\infty} = \frac{P}{RT}(2B_{ab} - B_{bb})$$

$$B_{ab} = \frac{1}{2}\left\{\left(\frac{RT}{P}ln\phi_a^{\infty}\right) + B_{bb}\right\} = -34.5\ cm^3/mole$$

- By geometric average:

$$\boxed{B_{ab} = \sqrt{B_{aa}B_{bb}} = -40.2\ cm^3/mole}$$

$B_{ab} \approx -32$

$B_{ab} \approx -34$

$B_{ab} \approx -40$

We have the other approach also. We have another equation also depending on in which form we are taking the equation that virial equation of state. Other form we are having $\ln \phi_i = \left(2\sum_{j=1}^{m} y_i B_{ij} - B_{mixt}\right)\frac{P}{RT}$. Now, here also if you take $y_a \to 0$, $y_b \to 1$, then you have $\ln \phi_a^{\infty}$ is equal to this expression. So, y_a is 0 here, so this term would be there, y_a is 0 here, so, y_a is 0 here, this term would be there and then $y_b = 1$. So, then what we can write, $\ln \phi_a^{\infty} = \frac{P}{RT}(2 B_{ab} - B_{bb})$ if you take $y_b = 1$, this is what we can write.

So, now here also, ϕ_a^{∞} is given, P is given, T is given, and then B_{bb} is given that is second virial coefficient of pure B is given. So, then we can obtain B_{ab}, only unknown, from this equation. So, that can be obtained as - 34.5 centimeter cube per mole. So, now, we can see here geometric average if you see, if you take geometric average also in the worst case, if the things are not available then you can take the geometric average, so B_{ab} if you take $\sqrt{B_{aa}B_{bb}}$.

So, it is coming - 40.2 centimeter cube per mole. So, now you can see here in our previous case what we have, it is approximately - 32 we got in the previous approach. This approach we got B_{ab} is approximately - 34 and then good thing to see the geometric average it is giving - 40, not very bad approximation considering the problem that we have, it is almost close to the values that we got by 2 different approaches. So, in the worst case when there is no information to find out cross virial coefficient if you know the pure virial coefficient, then we can find out cross virial coefficient by geometric average. This should be B_{bb}, right?

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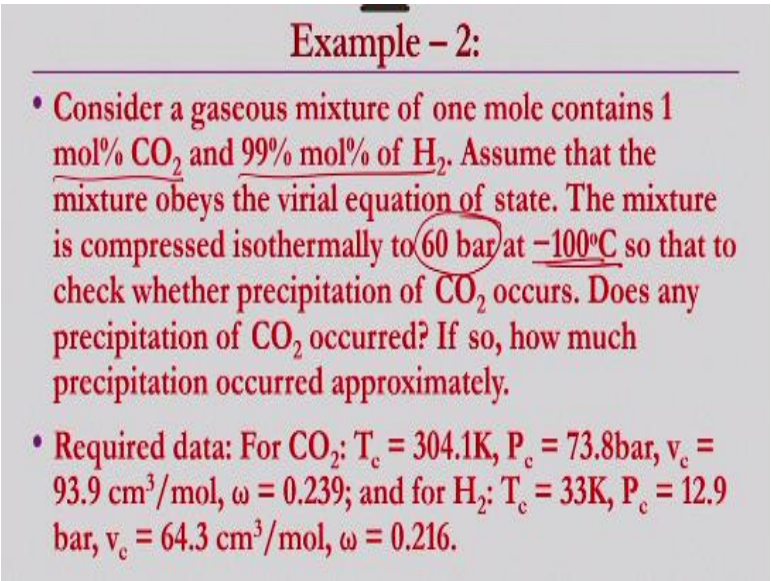

Example – 2:

- Consider a gaseous mixture of one mole contains 1 mol% CO_2 and 99% mol% of H_2. Assume that the mixture obeys the virial equation of state. The mixture is compressed isothermally to 60 bar at −100°C so that to check whether precipitation of CO_2 occurs. Does any precipitation of CO_2 occurred? If so, how much precipitation occurred approximately.
- Required data: For CO_2: $T_c = 304.1K$, $P_c = 73.8bar$, $v_c = 93.9\ cm^3/mol$, $\omega = 0.239$; and for H_2: $T_c = 33K$, $P_c = 12.9\ bar$, $v_c = 64.3\ cm^3/mol$, $\omega = 0.216$.

So, now we take another example problem. This problem actually we have seen in one of the lecture. This problem what we have taken, we have taken as a kind of example to find out the cross virial coefficient from different types of correlation that we have developed from the corresponding states of theory. So, those correlations we have used to find out the cross virial coefficients and then virial coefficients of pure systems, etc.

So now in addition to that we will be finding out now the fugacity of those components, okay? 2 components, and then further we try to find out what is real problem, then we get some information about the real problem. The real problem is that we have one mole gaseous mixture within which 1 mole percent is CO_2 and then 99 mole percent H_2 and then assume that these gaseous mixture obeys the virial equation of state and isothermally at - 100 degrees centigrade, this mixture is compressed to 60 bar so that to check whether precipitation of CO_2 occurs or not.

Out of this mixture CO_2 and H_2, we wanted to make H_2 much more pure. So, what we are doing? We are compressing this mixture to check whether this CO_2 is being compressed and then taken out as a kind of solid form or not. Once it is compressed as a kind of solid form, then we can easily separate it out from the H_2, so that H_2 to will become much more pure that is the purpose, right? So, that is what we wanted to check whether first of all if we compress isothermally at 60 bar, is it going to be precipitate or not?

If it is precipitating, how much it is precipitating that we have to find out. So, we have to use the virial equation of state. So, corresponding fugacity the expression we have to obtain, right because the virial coefficients are not given. So, this problem the data is given T_c, P_c, v_c for both the components are given and then ω also for both the components are given. So, using the correlation that we have seen in one of the previous lecture, so we will be finding the virial coefficients and those virial coefficients would be used in ln ϕ_i expression that we have derived today for virial equation of state.

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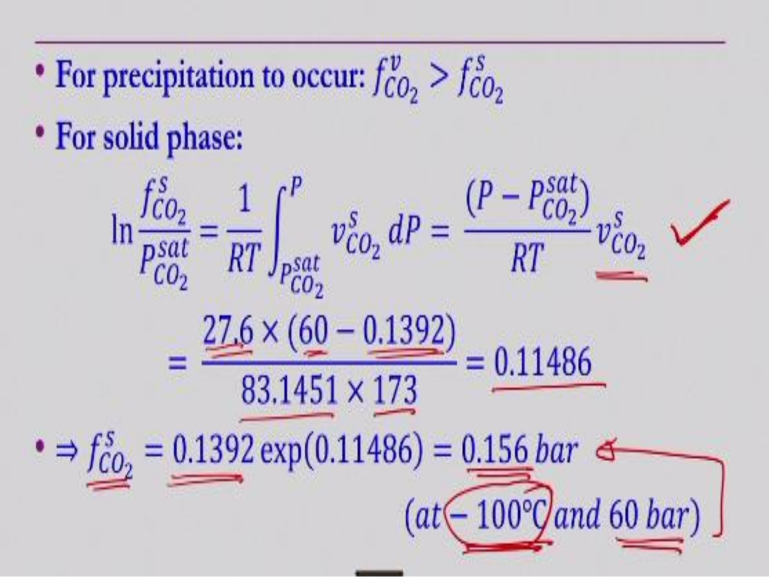

- For precipitation to occur: $f^{v}_{CO_2} > f^{s}_{CO_2}$
- For solid phase:

$$\ln\frac{f^{s}_{CO_2}}{P^{sat}_{CO_2}} = \frac{1}{RT}\int_{P^{sat}_{CO_2}}^{P} v^{s}_{CO_2}\,dP = \frac{(P - P^{sat}_{CO_2})}{RT}v^{s}_{CO_2}$$

$$= \frac{27.6\times(60 - 0.1392)}{83.1451\times 173} = 0.11486$$

- $\Rightarrow f^{s}_{CO_2} = 0.1392\exp(0.11486) = 0.156\,bar$

(at −100°C and 60 bar)

So, for precipitation to occur, what should be the condition? Precipitation in the sense initially gaseous mixture is there that we are bringing to the solid state. So, the chemical potential in the vapor phase if it is high, then you know that we will be transferring from high chemical potential to the low chemical potential side assuming the solid side, the compressed side is in kind of low chemical potential then precipitation will occur. So, what we have? We have gaseous mixture, right?

Now, we are compressing so that to there is a precipitation occur. If this has to occur, the certain component for CO_2 we are finding out. The chemical potential of CO_2 we have to find out or fugacity CO_2 we have to find out for either phases because they are equivalent. So, gaseous phase let us say f_{CO_2} we call it, for solid after precipitation if it all occurring $f^{s}_{CO_2}$ let us call. We have expression for the pure condensed component what is the fugacity expression.

So we can find out this one and then gaseous mixture it is given that it is given that virial equation of state is being obeyed by this gaseous mixture. So far the virial equation of state just now we have derived expression for fugacity coefficients. So, fugacity in the vapor phase also we can find out. So, if the chemical potential of this component is low in the gaseous mixture, so it cannot go from low chemical potential to the high chemical potential side, so the precipitation will not occur, right?

If the chemical potential of CO_2 in the gaseous phase is high, so then it is possible that from high chemical potential to the low chemical potential side that is solid side it can go, so then precipitation occur, right? So, you have to find out the chemical potential or chemical potential is much more clearly related to the fugacity, or fugacity and then you have to check which phase for this particular component fugacity you have to measure and then depending on in which phase it is high.

If it is high in the solid phase, so then it will not precipitate because it is already high fugacity solid state, so rather precipitating it may be going into the vapor state, gaseous state or if the fugacity of CO_2 is high in the vapor phase, so from high fugacity level to the low fugacity level the transfer of species will take place, right? So, then under such condition, precipitation will take place, okay? So, we have to find out these 2 information and then after finding out these 2 info values, then only we can see whether the precipitation is occurring or not.

Once we know the precipitation is occurring, we can find out how many moles are being precipitated that can also be found, okay? So, indirectly what has to be the condition, f_{CO_2} in vapor phase should be higher compared to the f_{CO_2} in the pure compressed solid state, okay? So, first solid phase pure and then assuming this compression is taking such a way that only CO_2 is precipitating, H_2 is not there, so that we can say that the solid phase is pure of CO_2 if it all precipitation is occurring, okay? That is the assumption, okay?

Only CO_2 is being compressed precipitated if at all it is occurring and H_2 is not being precipitated. Under such assumption what we can say if at all precipitation is occurring for the solid phase, it is going to be pure CO_2, pure solid CO_2, okay? Then we have already derived this expression long back you know second or third week for pure condensed phase, the fugacity you can find out using this expression.

What we have, we have this $v^s_{CO_2}$ is given as 27.6 or molar volume of CO_2 under the saturated conditions is given 27.6 and then P is given as 60 bar and then saturation pressure of CO_2 is given as 0.1392, in the problem statement it is given, otherwise we have to find out from the textbooks or we have to use the Antoine equation at this temperature whatever the - 127 temperature is there, at that temperature we have to find out corresponding saturation pressure from the Antoine equation using the Antoine constant A, B, C.

So, now everything is given here, R is known, so T is also given, so you can find it out this value as point 0.11486, So, then $f^s_{CO_2}$ would be nothing but whatever $P^s_{CO_2}$ is nothing but 0.1392, exponential of this value 0.11486 that is 0.156 bar. So, the fugacity of CO_2 in the solid precipitated form at this temperature of - 100 degrees centigrade and 60 bar, temperature is - 100 degrees centigrade, not the 127, okay?

At - 100 degrees centigrade and 60 bar, the fugacity of CO_2 if at all it is precipitating in a pure solid compressed state it is having 0.156 bars of fugacity. The same thing we have to find out for the vapor also that is gaseous mixture.

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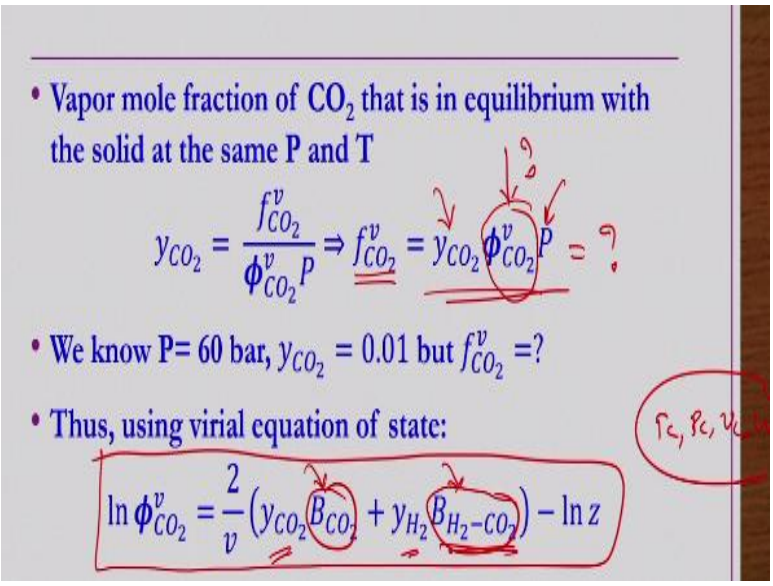

- Vapor mole fraction of CO_2 that is in equilibrium with the solid at the same P and T

$$y_{CO_2} = \frac{f^v_{CO_2}}{\phi^v_{CO_2} P} \Rightarrow \underline{\underline{f^v_{CO_2}}} = \underline{y_{CO_2}\phi^v_{CO_2} P} = ?$$

- We know P= 60 bar, $y_{CO_2} = 0.01$ but $f^v_{CO_2} = ?$
- Thus, using virial equation of state:

$$\boxed{\ln\phi^v_{CO_2} = \frac{2}{v}\left(y_{CO_2}B_{CO_2} + y_{H_2}B_{H_2-CO_2}\right) - \ln z}$$

For the vapor what we have, virial equation of state we are having, right? So, we know that $f^v_{CO_2} = y_{CO_2}\,\phi^v_{CO_2}$ P, y_{CO_2} is given, only 1 mole percent of CO_2 in the total mixture that is present, okay? And then P is also given 60 bar. So, $\phi^{v}_{CO_2}$ if you find out, then you can find out how much is $f^{v}_{CO_2}$ by using this expression and then depending on this value how much it is you can decide whether precipitation is occurring more or not. If this value $f^{v}_{CO_2}$ is higher than the $f^{s}_{CO_2}$, then precipitation would occur, okay?

So, but in order to find out this one, we have to use the ln ϕ expression for the virial equation of state that we have derived just now, right? So, that expression if you write for a binary component whatever the expression is there that you expand for H_2 and then CO_2, so we need only for CO_2 H_2 we do not want, so we do not want to calculate anyway. So, ln $\phi^{v}_{CO_2} = \frac{2}{v}$ y_{CO_2} B_{CO_2} + y_{H_2} $B_{H_2-CO_2}$ - ln z, y_{CO_2} is nothing but mole fraction of CO_2 in the mixture and then y_{H_2} is nothing but mole fraction of H_2 in the mixture.

B_{CO_2} is nothing but second virial coefficient of pure CO_2 and then $B_{H_2-CO_2}$ is nothing but the cross virial coefficient of H_2 CO_2. So, how to find out these things? Without these information, we cannot solve this problem, but in one of the previous lecture, we have found this thing using the correlations because for these components T_c, P_c, v_c, ω these information are available.

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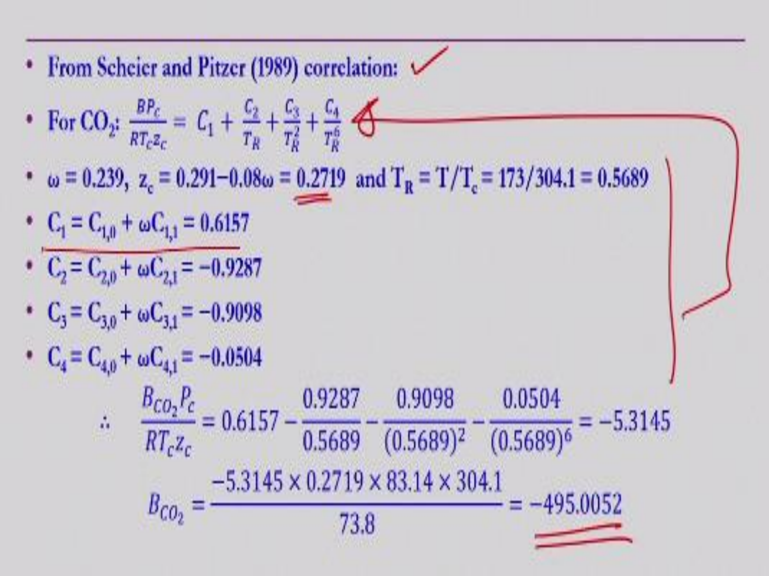

- From Scheier and Pitzer (1989) correlation: ✓
- For CO_2: $\frac{BP_c}{RT_c z_c} = C_1 + \frac{C_2}{T_R} + \frac{C_3}{T_R^2} + \frac{C_4}{T_R^6}$
- $\omega = 0.239$, $z_c = 0.291 - 0.08\omega = 0.2719$ and $T_R = T/T_c = 173/304.1 = 0.5689$
- $C_1 = C_{1,0} + \omega C_{1,1} = 0.6157$
- $C_2 = C_{2,0} + \omega C_{2,1} = -0.9287$
- $C_3 = C_{3,0} + \omega C_{3,1} = -0.9098$
- $C_4 = C_{4,0} + \omega C_{4,1} = -0.0504$

$$\therefore \quad \frac{B_{CO_2} P_c}{RT_c z_c} = 0.6157 - \frac{0.9287}{0.5689} - \frac{0.9098}{(0.5689)^2} - \frac{0.0504}{(0.5689)^6} = -5.3145$$

$$B_{CO_2} = \frac{-5.3145 \times 0.2719 \times 83.14 \times 304.1}{73.8} = -495.0052$$

So, that we have used and then we found these coefficients already, so but however, I am putting them here once again as a kind of recapitulation. So, for CO_2 we have used this correlation by Scheier and Pitzer, right? So, here C_1, C_2, C_3, C_4 are functions of ω, right? Ω is given for CO_2 and z_c is again a function of ω, so z_c you can find out. T_R is nothing but $\frac{T}{T_c}$, T_c is given, T is given as - 100 degrees centigrade. So then the T_R you can find out. So, except C_1, C_2, C_3, everything is known here.

C_1 we can find out using this correlation according to them, like C_2 also we can find out, C_3 and C_4 also we can find out. Then when you substitute this information here in this expression, all this information if you substitute here in this expression, then you will get B_{CO_2} as - 495 centimeter cube per mole roughly. I am just going forward quickly because this problem we have already solved in one of the reaction only this part of the problem that is finding cross virial coefficient.

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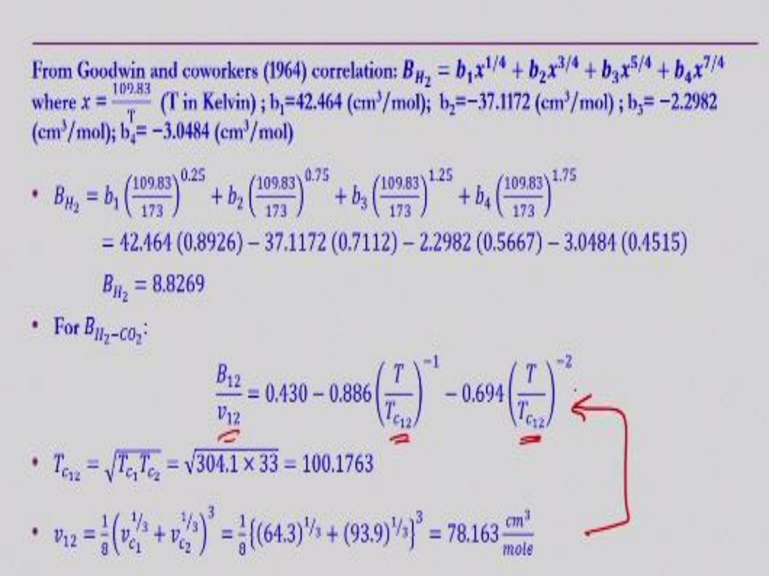

From Goodwin and coworkers (1964) correlation: $B_{H_2} = b_1 x^{1/4} + b_2 x^{3/4} + b_3 x^{5/4} + b_4 x^{7/4}$ where $x = \frac{109.83}{T}$ (T in Kelvin) ; b_1=42.464 (cm³/mol); b_2=−37.1172 (cm³/mol) ; b_3= −2.2982 (cm³/mol); b_4= −3.0484 (cm³/mol)

- $B_{H_2} = b_1\left(\frac{109.83}{173}\right)^{0.25} + b_2\left(\frac{109.83}{173}\right)^{0.75} + b_3\left(\frac{109.83}{173}\right)^{1.25} + b_4\left(\frac{109.83}{173}\right)^{1.75}$
  $= 42.464\,(0.8926) - 37.1172\,(0.7112) - 2.2982\,(0.5667) - 3.0484\,(0.4515)$
  $B_{H_2} = 8.8269$
- For $B_{H_2-CO_2}$:
  $$\frac{B_{12}}{v_{12}} = 0.430 - 0.886\left(\frac{T}{T_{c_{12}}}\right)^{-1} - 0.694\left(\frac{T}{T_{c_{12}}}\right)^{-2}$$
- $T_{c_{12}} = \sqrt{T_{c_1} T_{c_2}} = \sqrt{304.1 \times 33} = 100.1763$
- $v_{12} = \frac{1}{8}\left(v_{c_1}^{1/3} + v_{c_2}^{1/3}\right)^3 = \frac{1}{8}\{(64.3)^{1/3} + (93.9)^{1/3}\}^3 = 78.163\,\frac{cm^3}{mole}$

Similarly, for H_2 we have this correlation by Goodwin and co-workers that is B_{H_2} = $b_1 x^{1/4}$ + $b_2\, x^{3/4}$ + $b_3\, x^{5/4}$ + $b_4\, x^{7/4}$. This b_1, b_2, b_3, b_4 are constants are available as per this correlation and the x is also given as per correlation 109.83 divided by T, T should be taken in Kelvin. When you substitute all these numbers here, then you will get B_{H_2} is approximately 8.8269 centimeter cube per mole and for cross virial coefficient, we will be using the McGlashan correlation.

So, that is given like this here, so we need $T_{c_{12}}$ and then v_{12}. So these things $T_{c_{12}}$ we know that square root of T_{c_1} T_{c_2}, $v_{c_{12}}$ is nothing but $\frac{1}{8}\left(v_{c_1}^{1/3} + v_{c_2}^{1/3}\right)^3$, then we get v_{12} this one, right?

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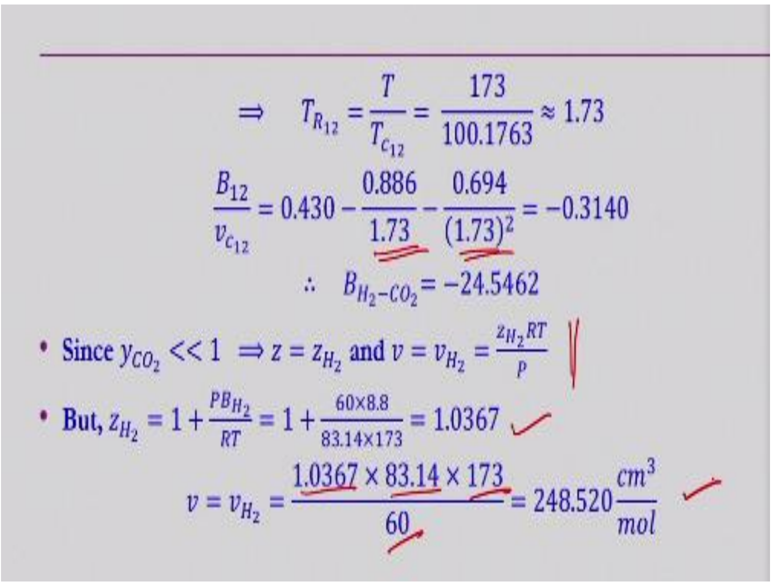

$$\Rightarrow T_{R_{12}} = \frac{T}{T_{c_{12}}} = \frac{173}{100.1763} \approx 1.73$$

$$\frac{B_{12}}{v_{c_{12}}} = 0.430 - \frac{0.886}{1.73} - \frac{0.694}{(1.73)^2} = -0.3140$$

$$\therefore B_{H_2-CO_2} = -24.5462$$

- Since $y_{CO_2} << 1 \Rightarrow z = z_{H_2}$ and $v = v_{H_2} = \frac{z_{H_2}RT}{P}$
- But, $z_{H_2} = 1 + \frac{PB_{H_2}}{RT} = 1 + \frac{60\times 8.8}{83.14\times 173} = 1.0367$

$$v = v_{H_2} = \frac{1.0367 \times 83.14 \times 173}{60} = 248.520 \frac{cm^3}{mol}$$

So if you substitute this information here in this expression, you will get v_{12} as. Next $T_{R_{12}}$ is nothing but 1.73 and then $\frac{B_{12}}{v_{c_{12}}}$ if you use this expression $T_{R_{12}}$ expression in previous this correlation, in this correlation here, this $\frac{T}{T_{c_{12}}} = T_{R_{12}}$. So, that information if you use here in this correlation T_R^{-1} T_R^{-1}, so that we use here and then $v_{c_{12}}$ also we got, so then $B_{H_2-CO_2}$ second cross virial coefficient of H_2 CO_2 at this temperature of - 100 degrees centigrade is nothing but - 24.5462 centimeter cube per mole.

So, you have all the information and then in the mixture the CO_2 is present in very small, only 1 mole percent, right? So, then we can say that whatever the mixture is there almost pure H_2. If you take that logic, then you can say z_{mixt} is nothing but z_{H_2} and then v_{mixt} is nothing but v_{H_2} because these two information we need in order to find out this fugacity ln $\phi_{CO_2}^{v}$ that expression we need v_{mixt} and z_{mixt} also. So, we do not have any other way of calculating it except using the logic of the problem given that is the CO_2 is very small.

So, then we can take remaining component H_2 as a kind of dominating in the mixture. So, that mixture may be approximated as a kind of a pure H_2 in order to guess this z and then v for the mixture. So $z_{H_2} = 1 + \frac{PB_{H_2}}{RT}$, B_{H_2} we got 8.8 something, P is 60 bar, T is - 100 degrees centigrade. So, then we get z_{H_2} as 1.0367. Similarly, v_{H_2} if you have z_{H_2}, then v_{H_2} we can write it as you know $z_{H_2} \frac{RT}{P}$, z_{H_2} is 1.0367. This is R, this is T, this is P, so v_{H_2} we will get 248.520 centimeter cube per mole.

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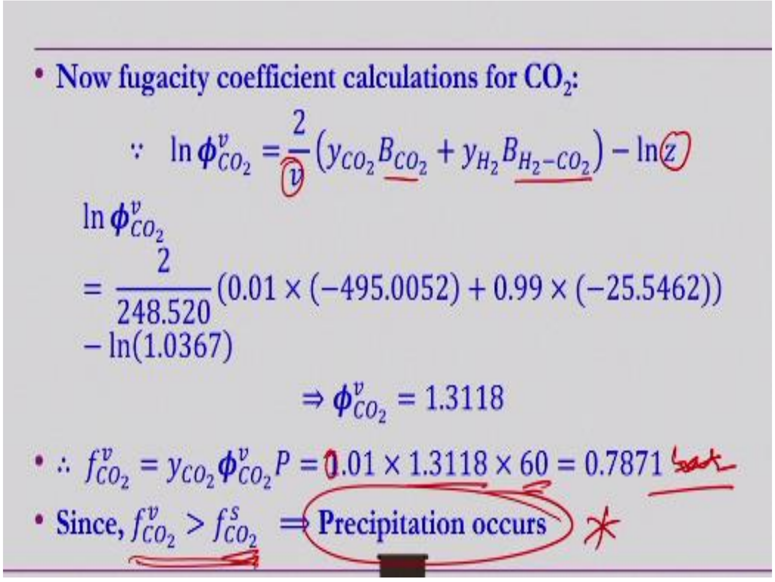

- Now fugacity coefficient calculations for CO$_2$:

$$\because \ \ln \phi^v_{CO_2} = \frac{2}{v}\left(y_{CO_2}\underline{B_{CO_2}} + y_{H_2}\underline{B_{H_2-CO_2}}\right) - \ln z$$

$$\ln \phi^v_{CO_2} = \frac{2}{248.520}(0.01 \times (-495.0052) + 0.99 \times (-25.5462)) - \ln(1.0367)$$

$$\Rightarrow \phi^v_{CO_2} = 1.3118$$

- $\therefore f^v_{CO_2} = y_{CO_2}\phi^v_{CO_2}P = 0.01 \times 1.3118 \times 60 = 0.7871$ bar
- Since, $f^v_{CO_2} > f^s_{CO_2} \Rightarrow$ Precipitation occurs *

So now, we got all the information to find out ln $\phi^v_{CO_2}$, v also, v_{mixt} we got, z_{mixt} we got, cross virial coefficients and pure component virial coefficients also we got. So substitute them here. Then we get $\phi^v_{CO_2}$ as 1.3118. So from here, $f^v_{CO_2}$ = y_{CO_2} $\phi^v_{CO_2}$ P that we got. So then y_{CO_2} is nothing but 0.01, right? And then $\phi^v_{CO_2}$ is 1.3118 and then P is 60 bar, so then you get $f^v_{CO_2}$ is nothing but 0.7871 bar and then it is very much higher compared to the $f^s_{CO_2}$, so the precipitation will occur, okay?

So, now we found precipitation is occurred, but how much it occurred, if that you wanted to know, what is the mole fraction of this particular component in either of the phases at equilibrium we have to find out. We have seen that these are not equal $f^v_{CO_2}$ and $f^s_{CO_2}$ they are not equal, so then we realize that the precipitation has occurred, some process compression has taken place, okay? But otherwise not necessary that if you maintain the constant temperature and then increase the pressure all the system will go some kind of compression, it depends on the system to system.

For this system, the compression of CO$_2$ has taken place. So, if you wanted to know how many moles of compression has taken place, you have to know the composition at the equilibrium, right?

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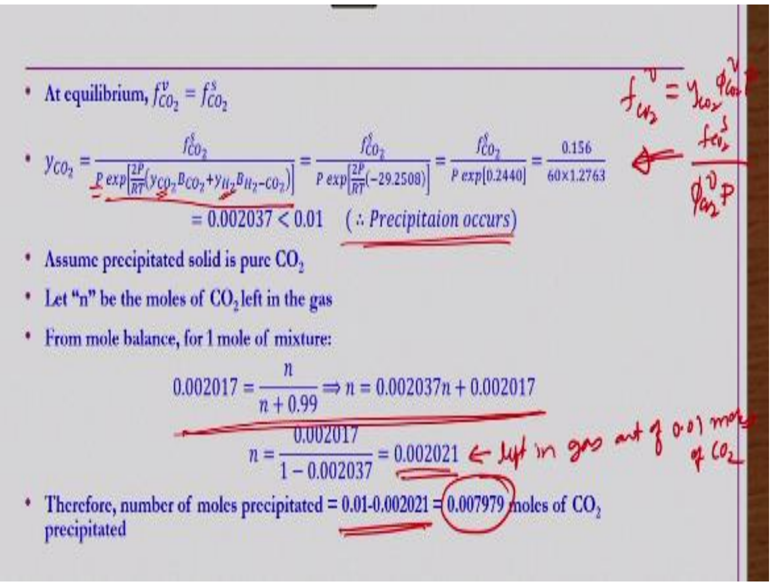

- At equilibrium, $f^v_{CO_2} = f^s_{CO_2}$
- $y_{CO_2} = \frac{f^s_{CO_2}}{P\exp\left[\frac{2P}{RT}(y_{CO_2}B_{CO_2}+y_{H_2}B_{H_2-CO_2})\right]} = \frac{f^s_{CO_2}}{P\exp\left[\frac{2P}{RT}(-29.2508)\right]} = \frac{f^s_{CO_2}}{P\exp[0.2440]} = \frac{0.156}{60\times1.2763}$
  $= 0.002037 < 0.01$ ($\therefore$ *Precipitaion occurs*)
- Assume precipitated solid is pure CO_2
- Let "n" be the moles of CO_2 left in the gas
- From mole balance, for 1 mole of mixture:

$$0.002017 = \frac{n}{n+0.99} \Rightarrow n = 0.002037n + 0.002017$$

$$n = \frac{0.002017}{1-0.002037} = 0.002021$$

← left in gas out of 0.01 moles of CO_2

- Therefore, number of moles precipitated = 0.01-0.002021 = 0.007979 moles of CO_2 precipitated

$f^v_{CO_2} = y_{CO_2}\phi^v_{CO_2}$

$\frac{f^s_{CO_2}}{\phi^v_{CO_2}P}$

So, at equilibrium what we know $f^v_{CO_2} = f^s_{CO_2}$, $f^s_{CO_2}$ is a constant one that we already got it as 0.156 and then $f^v_{CO_2} = y_{CO_2}\ \phi^v_{CO_2}$P, this is what we know. So, then from here we can find it out $y_{CO_2} = f^s_{CO_2}$ divided by $\phi^v_{CO_2}$ P. So, P and then $\phi^v_{CO_2}$ is nothing but $\exp\left[\frac{2P}{RT}\left(y_{CO_2}B_{CO_2} + y_{H_2}B_{H_2-CO_2}\right)\right]$, this is what we got, right?

So, now here if you substitute this for the mixture whatever the y_{CO_2} etc of all these mixtures for the mixture composition if you substitute 0.01 and then 0.99, then you will be able to find out what is the y_{CO_2} at the equilibrium, whatever the inequality is there because of this y_{CO_2} is going into the different phase. So, how much it has gone, so you can find out by this one. So, that is 0.002037 is coming. If at all it is equilibrium, no precipitation has occurred, so then y_{CO_2} we should have got back to its initial value of 0.01, if no precipitation has occurred, only gaseous phase is there.

So, then y_{CO_2} has to be 0.01 at equilibrium as well, but at equilibrium y_{CO_2} is not equals to 0.01 of initial value, it is much lesser, 0.002. So, that means some amount is there that is being precipitated, okay? That we have to find out. So, by this way also we can find out that precipitation has occurred by comparing the y_{CO_2} value at equilibrium with the y_{CO_2} in the feed or the initial y_{CO_2}. Initial y_{CO_2} and then y_{CO_2} at equilibrium are not same, that means some transfer of the species has taken place, okay?

Now, here transfer of species is taking place from a gaseous phase to the compressed CO_2 phase. So, now assume precipitated solid is pure CO_2 and let n be the moles of CO_2 left in the gas, then from mole balance for 1 mole of mixture, we can have this expression that whatever the y_{CO_2} at equilibrium should be equals to $\frac{n}{n}$ + whatever the mole fraction of other component, then you can find it out n as nothing but 0.002021, these many moles are left in the gas out of 0.01 moles of CO_2.

Total 1 mole of gas there out of which only 0.01 moles CO_2 are there, but after this compression only 0.002 moles of CO_2 is remaining. So, remaining amount whatever is there, remaining amount 0.008, approximately 0.008 moles of CO_2 has been precipitated. So this is how we can solve any real-life problem. In the next lecture, we will be taking a few more examples to understand how to make use of this fugacity information to solve a few real-life equilibrium problems, okay?

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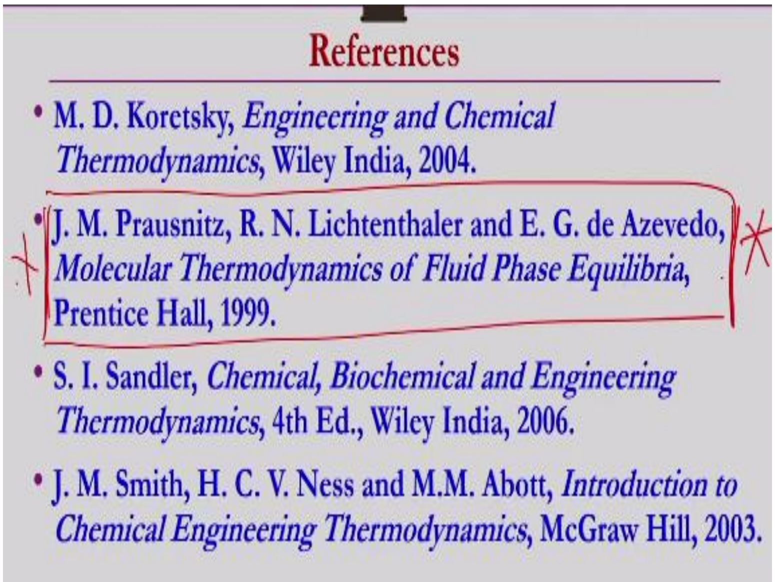

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- J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, *Molecular Thermodynamics of Fluid Phase Equilibria*, Prentice Hall, 1999.
- S. I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics*, 4th Ed., Wiley India, 2006.
- J. M. Smith, H. C. V. Ness and M.M. Abott, *Introduction to Chemical Engineering Thermodynamics*, McGraw Hill, 2003.

So, the references for this particular lecture are given here. Engineering and Chemical Thermodynamics by Koretsky. Molecular Thermodynamics of Fluid Phase Equilibria by Prausnitz et al. Chemical, Biochemical and Engineering Thermodynamics by Sandler and then Introduction to Chemical Engineering Thermodynamics by Smith et al. The problems that have been solved here are the kind of exercise problems given in this particular book.

Also the virial equation of state and their corresponding fugacity expressions are also provided in this particular book. So, this is going to be important reference book for this particular lecture. Thank you.