Advanced Thermodynamics
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Lecture – 5
Fugacity from Volumetric Data

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is Fugacity from Volumetric Data. In the previous lecture, we have seen how to estimate thermodynamic properties if volumetric information or volumetric measurements are available, right? So, this lecture is a bit continuation of a previous lecture. So, what we do, we have a kind of recapitulation of previous lecture.

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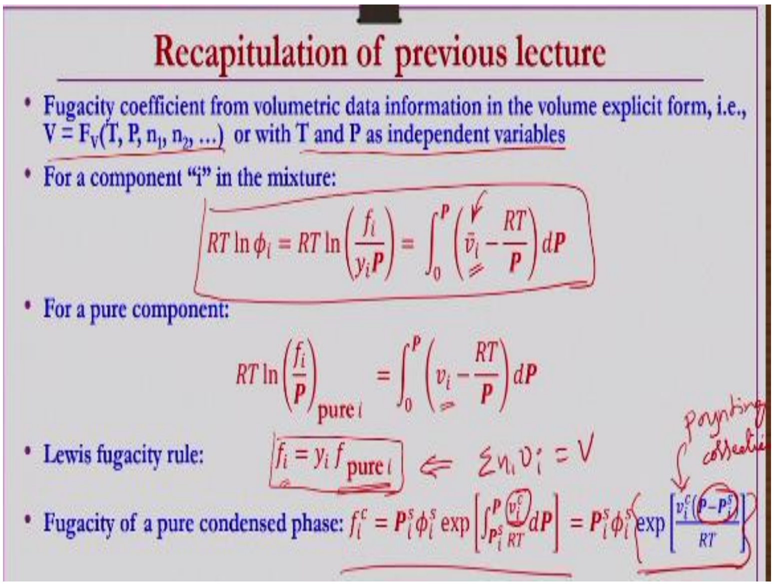

We have seen primarily how to estimate thermodynamic properties like U, V, s, h, A, G, etc., provided if you know V as function of temperature, pressure, and composition or as temperature and pressure are independent variables, under such conditions if you know the volumetric information, then how to estimate the thermodynamic properties, those things we have seen. In addition to that one, we have also seen how to estimate fugacity of a component i in a mixture if we know the volumetric data information in the form of volume explicit form.

That is V as function of temperature, pressure, and composition or otherwise if we know the volumetric data and then if you have a temperature and pressure as independent variables then how to measure thermodynamic properties, those things we have seen. Then in addition to that one, we have also seen how to estimate fugacity coefficient for non-ideal systems, how to estimate the fugacity coefficient or fugacity for a component in a mixture or a pure component that we have seen temperature and pressure as independent variables, right?

Then we derived for a component i in the mixture fugacity coefficient can be estimated using this expression that is RT ln $\phi_i = \int_0^P \left(\bar{v}i - \frac{RT}{P}\right) dP$. So, whatever the volumetric data information is available in volume explicit form that what we do? We obtain the partial molar volume of i^{th} component for which we wanted to measure fugacity and then substitute here, do the simplification, so then we get fugacity coefficient of that i^{th} component in the mixture.

So, we have also taken an example of Van der Waal's equation and then we derived what is the fugacity coefficient ϕ_i for a component i in a mixture of gases which obey Van der Waal's equation of state. Then for a pure component also we have derived these relations that is RT ln $\left(\frac{fi}{P}\right)_{pure\ i} = \int_0^P \left(\bar{v}i - \frac{RT}{P}\right) dP$. Here simply, we are having v_i in case of pure component because for pure component partial molar volume is nothing but its molar volume, right?

Then also we have derived this Lewis fugacity rule which is true when we mix the component in such a way that there is no change in total volume fugacity of component i in the mixture you can know directly without doing any calculation if you know fugacity of the same component as if it is a pure component simply by multiplying the volume fraction of that particular component in the mixture you will get fugacity of that particular component in the mixture that is $f_i = y_i\ f_{pure\ i}$.

f_i is nothing but fugacity of component i in the mixture, $f_{pure\ i}$ is nothing but fugacity of that same i^{th} component but as a kind of pure state, it is not mixed with anything. So, this derivation we have seen and then also for fugacity of a pure condensed phase we have direct this relation $f_i^c = P_i^s\ \phi_i^s\ \exp\left[\int_{P_i^s}^{P} \frac{v_i^c}{RT} dP\right]$, P_i^s is nothing but the saturation pressure. Below the saturation pressure you know vapor form is there and then beyond the saturation pressure, the condensed liquid form maybe there, right?

So, then at the saturation pressure, these 2 phases would be at equilibrium, right? ϕ_i^s nothing but the fugacity of that particular pure component, but under the saturation vapor conditions, okay? Or ϕ_i^s is nothing but the fugacity of a saturated vapor. And then if we have made an assumption that you know if the conditions are, the pressure changes ΔP is far away from the critical range or saturation pressure, etc., are far away from the critical conditions of the system, then we can say that v_i^c that is the molar volume of the condensed phase is independent of the pressure or the condensed pressure is incompressible.

Then we can simply integrate this one as you know v_i^c as independent of pressure and then we have this exponential correction, $\exp\left[\frac{v_i^c(P-P_i^s)}{RT}\right]$ and this we named it as this particular thing we call it as Poynting corrections. We have also seen how much important it is, it depends on what is ΔP, $\Delta P = P - P_i^s$, P is beyond the saturation pressure then only there will be a kind of condensed phase but if the P is below the saturation pressure at given temperature then we will not be having a kind of condensed phase, we will be having a saturated vapor kind of thing, okay?

So, depending on the magnitude of this ΔP, we can say how much important is this fugacity correction. We have seen let us say if v_i^c is approximately 100 cc per mole, then we can say this ΔP is less than 10 bar, this Poynting correction is almost negligible that is what we have already seen.

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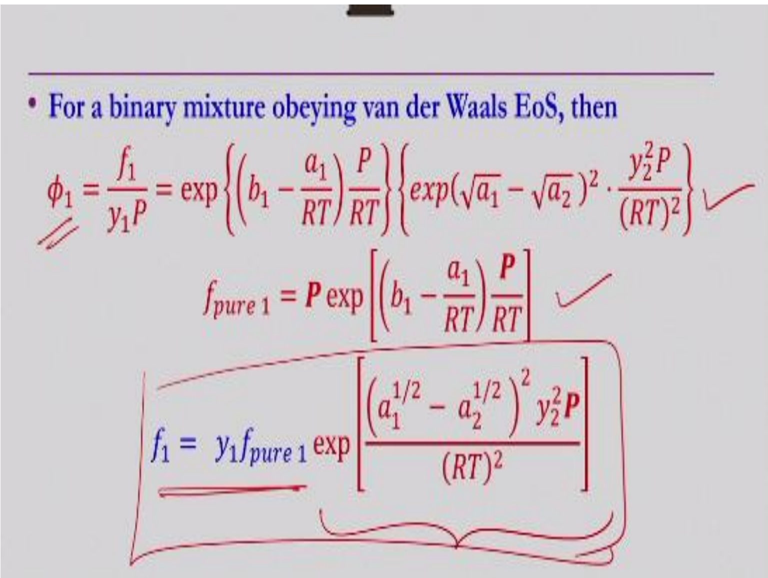

Then for a binary mixture obeying Van der Waal's equation of state then we have found this fugacity coefficient of first component ϕ_1 as this one, this is what we have derived and then for pure component obeying same Van der Waal's equation we have derived this relation and then we made a kind of connection between these 2 equations and then we have written like this equation $f_1 = y_1 f_{pure\ 1}$ and then multiplied by this exponential factor.

This exponential factor is coming additional as a kind of you know correction to the Lewis fugacity rule. If you recollect $f_i = y_i f_{pure\ i}$ is nothing but the Lewis fugacity rule there is a correction here. This is what we have seen in our previous lecture. Now, what we do? We take a few example problems based on what we have seen the fugacity calculations, etc. from volumetric information if temperature and pressure as kind of independent variables, those things we have derived. Based on those things, now we see a few example problems.

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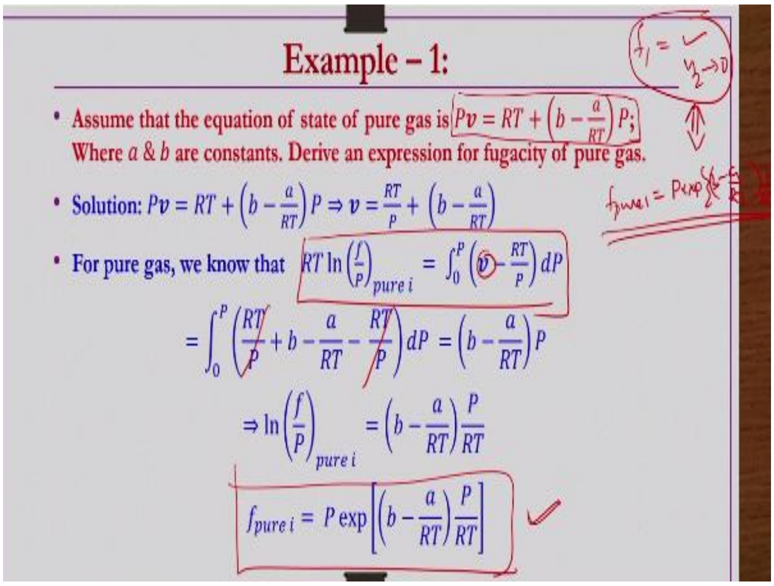

Example 1. Assume that the equation of state of pure gas is $Pv = RT + \left(b - \frac{a}{RT}\right)P$ where a and b are constants. Derive an expression for fugacity of pure gas. Actually this is nothing but the Van der Waal's equation that we have already seen in the previous case and then these a and b are a kind of you know Van der Waal's constants, right? We have derived $f_{pure\ 1}$ by substituting in f_1, y_2 tends to 0. Like what we have done, we have got f_1 expression for a Van der Waal's equation and then we substituted y_2 tends to 0.

Actually, if you remember this is having 2 corrections, 2 exponential correction, second correction is having y_2 term. So, that y_2 term goes off and then only first exponential term we have. So, then what we got, $f_{pure\ 1}$ is nothing but $P \exp\left[\left(b - \frac{a}{RT}\right)\frac{P}{RT}\right]$, this is what we have derived, right? This we derived by substituting here in this expression y_2 tends to 0 or $y_2 = 0$

that we substitute we got it. But let us say if you do not have this f_1 relation then how do you get $f_{pure\ 1}$? Right?

So, that is what simply we are taking a kind of starting example problem for simplicity as well as cross checking. This equation of state we have to write in volume explicit form. So, when you write it, we have $\frac{RT}{P} + b - \frac{a}{RT}$ as v and then for pure component, we have already derive this relation that RT $\ln\left(\frac{f}{P}\right)_{pure\ i} = \int_0^P \left(v - \frac{RT}{P}\right) dP$. So, simply here in place of v you substitute $\frac{RT}{P} + b - \frac{a}{RT}$, then we have this thing, so, $\frac{RT}{P}$, $\frac{RT}{P}$ cancelled out.

So, then we have $\left(b - \frac{a}{RT}\right)P$, this is what we have. So, then $\ln\left(\frac{f}{P}\right)_{pure\ i} = \left(b - \frac{a}{RT}\right)\frac{P}{RT}$ this left hand side whatever RT is there we are bringing into the right hand side. Then, $f_{pure\ i}$ is nothing but P $\exp\left[\left(b - \frac{a}{RT}\right)\frac{P}{RT}\right]$ and this is same expression as the one that we have derived from f_1, in f_1 relation that we derived in previous class for Van der Waal's equation, a binary mixture obeying Van der Waal's equation of state that we have consider and then we have derived f_1 relation.

In f_1 relation, by substituting y_2 tends to 0, then since it is a binary mixture if y_2 tends to 0, then it is a pure one. So then for that case, $f_{pure\ 1}$ we derived like this and then let us say the pure we do not know what is that f_1 for a binary mixture. Then from the pure expression for pure gas whatever the fugacity expression is there that we made use and then we got the same thing, so that a kind of practice as well as a crosscheck.

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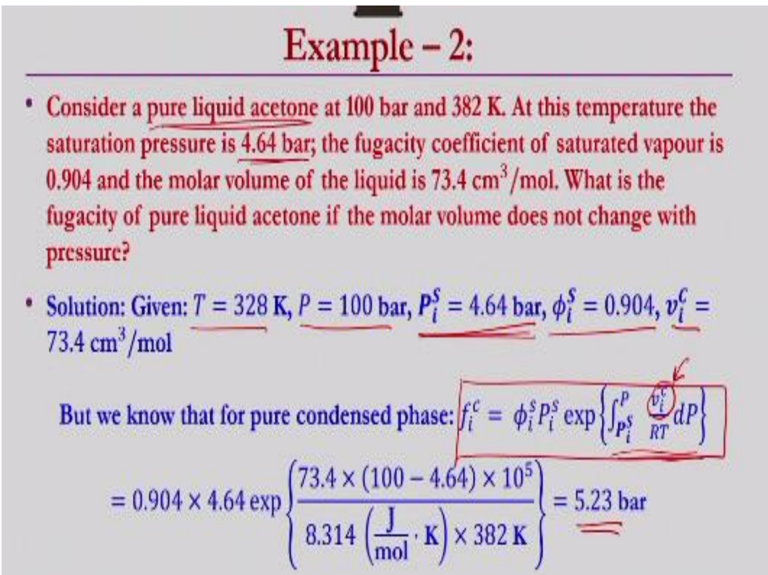

Now, we take another example problem. Consider a pure liquid acetone at 100 bar and 382 Kelvin. At this temperature this saturation pressure is 4.64 bar. The fugacity coefficient of saturated vapor that is ϕ_i^s is nothing but 0.904 and then molar volume of the liquid that is condensed phase v_i^c is nothing but 73.4 cc per mole. What is the fugacity of pure liquid acetone if the molar volume does not change with pressure? The pure acetone is in the liquid form that is in the pure condensed form, right? That means then whatever fugacity or relation that we have developed for a pure condensed phase that we have to use, okay?

So, before solving the problem, let us just list out what has been given. Temperature is given, pressure is given and saturation pressure is given that means $\Delta P = P - P_i^s$ is given. Fugacity coefficient of saturated vapor is given ϕ is, so that is given. Molar volume of the condensed phase v_i^c is given. So, simply substitute them in this equation that we have derived in previous lecture, v_i^c is independent of the pressure difference and then we can say that it is a kind of incompressible condensed way.

So, then we can integrate this particular part without worrying whether v_i^c is dependent on the pressure or not because we have seen that it is independent of a pressure for incompressible phase. Then, we get $\frac{v_i^c}{RT}$ dP. So, that is what we have. Substitute all these quantities because everything is known then we get fugacity of condensed phase that is pure acetone is nothing but 5.23 bar, okay? Since it is a kind of pure acetone, at this condition this pure acetone is in the liquid form.

So, then that is you know beyond the saturation pressure. So, obviously as a crosscheck what you can see whether the fugacity is coming beyond the saturation pressure value or not. If you are getting the value f_i^c below the or equal to the P_i^s then that means you are making some mistakes in the calculations because it is a pure acetone, is in the condensed form and then so obviously, its fugacity which is nothing but the corrected pressure that should be beyond the saturation vapor pressure that is beyond 4.64 bar. So, then we are we are getting higher than that value, okay?

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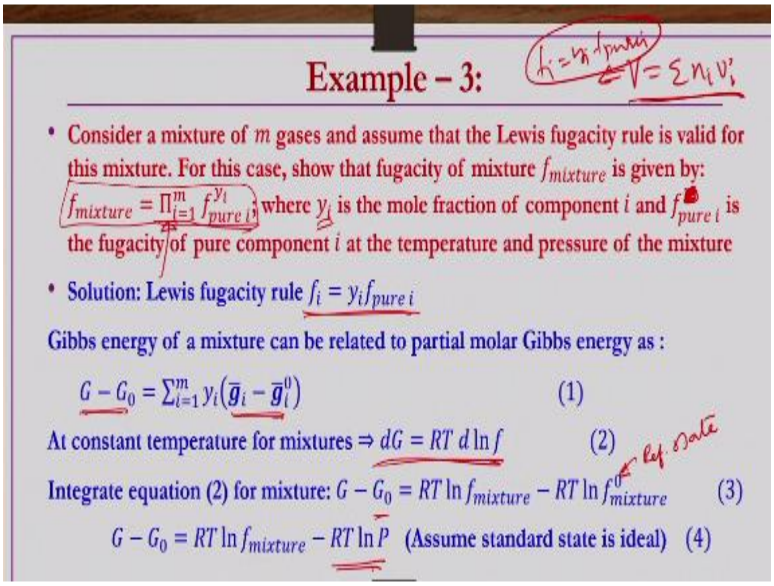

Then, another example problem. Consider a mixture of m gases and assume that the Lewis fugacity rule is valid that is $V = \Sigma n_i v_i$ or $f_i = y_i f_{pure\,i}$ that is also known. So, fi = $y_i f_{pure\,i}$, this is what the Lewis fugacity rule in terms of figures, okay? Whereas this $V = \Sigma n_i v_i$ is nothing but Amagat's law. So, far this case shows that the fugacity of mixture, $f_{mixture} = \Pi_{i=1}^{m} f_{pure\,i}^{yi}$ this is what we have to prove, right? And then here this Π is nothing but the product.

Like Σ we take for this summation, now here in this case this Π is for the product. So, where here in this expression y_i is nothing but the mole fraction of component i and then $f_{pure\,i}$ is the fugacity of pure component i at the temperature and pressure of the mixture this is what we have to prove. So, but what we have Lewis fugacity rule is nothing but $f_i = y_i f_{pure\,i}$, this will be using somewhere later stage right? Let us make note of it and then keep it here as it is.

Gibb's energy of a mixture can be related to partial molar Gibb's energy, $G - G_o = \Sigma y_i (\bar{g}_i - \bar{g}_i^{\circ})$, so small letters we are using for the molar properties and then bar is for the partial molar properties, okay? And then capital letters we are using for the total properties that is what symbols we are following for this lectures. In the previous lecture also, we followed the same thing. So, now, what we have to do? We have to make a relation what is $G - G_o$ for a mixture in terms of fugacity.

Similarly, we have to make a relation what is $\bar{g}_i - \bar{g}_i^{\circ}$ for i[th] competent in the mixture, substitute them here, simplify, then you will get the relation. And it is quite straightforward and simple because we know dG is nothing but RT dln f. If you apply this expression for a mixture, then we will have $G - G_o = dG = RT \ln f_{mixture} - RT \ln f^{\circ}_{mixture}$, this ° is a reference state, okay? Or some reference standard temperature and pressure that we take as a kind of reference because we calculate this thing related to some reference state, okay?

G_o is nothing but Gibbs energy at that reference state. So, we take reference state as ideal gas and then if the gaseous mixture is a kind of ideal gas, then fugacity of that mixture should be total pressure simply, okay? Then we get here RT ln P, right?

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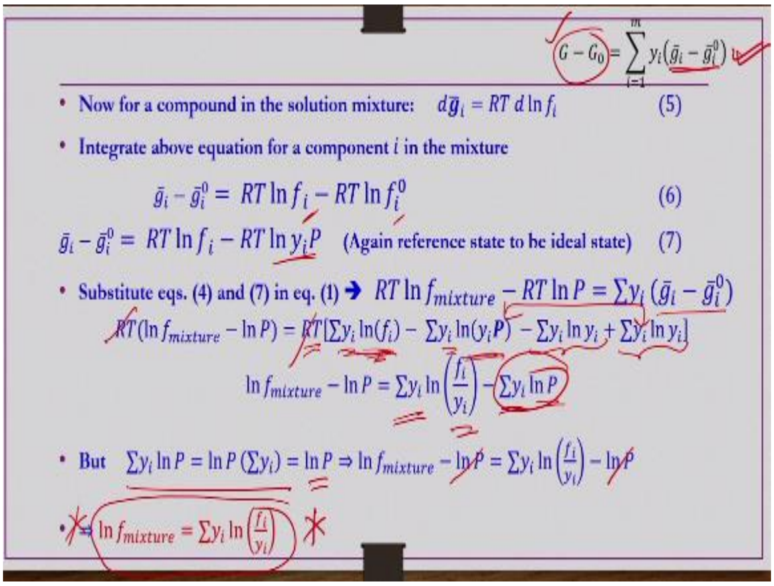

So, now the same expression here in this part this is known. So, now similarly we apply dG = RT dln f expression further $\bar{g}_i - \bar{g}_i^{\circ}$, okay? When you apply this one $d\bar{g}_i = RT\, d\ln f_i$, right? So, then for the i^{th} component in the mixture $\bar{g}_i - \bar{g}_i^{\circ} = RT \ln f_i - RT \ln f_i^{\circ}$. Now, i^{th} component we are writing, we are not writing for the mixture, so that is the reason f_i, f_i° are there. And then for one equation, we cannot have two different reference states.

So, here also we have to take reference state as a kind of ideal gas at low pressure and certain temperature T and then if that is the case, then for ideal gas mixture fugacity of i^{th} component in the mixture is nothing but the partial pressure of that component. So, that means f_i° is nothing but $y_i P$. So, that we substitute here. So, now we know $G - G_o$ we know, $\bar{g}_i - \bar{g}_i^{\circ}$ also we know. So, we can substitute them in this equation and then simplify. So, this is what we have $RT \ln f_{mixture} - RT \ln P = \Sigma\, y_i (\bar{g}_i - \bar{g}_i^{\circ})$.

That means, this $\bar{g}_i - \bar{g}_i^{\circ} = RT \ln f_i - RT \ln y_i P$, right? But this $\bar{g}_i - \bar{g}_i^{\circ}$ is multiple y_i. So, then these both the terms $\ln f_i$ $\ln y_i P$ should be multiplied by y_i and then there should be summation, okay? And then RT we are taking common. Now, this part what we do? We add RT Σ y_i ln y and then we subtract same quantity RT Σ y_i ln y, RT we have taken outside as common just for simplicity, okay? As well you know we have a relation that $\frac{fi}{yi\ P}$ kind of things we need actually, okay?

So, then now what we do? Our next step we combine these 2 terms and then we combine remaining these 2 terms. Then, what we get? Then, we get ln $f_{mixture}$ - ln P=Σy_i ln $\frac{fi}{yi}$ - Σy_i ln$\frac{yiP}{yi}$. So y_i, y_i cancelled out, so ln P we are getting this one from remaining 2 terms and then RT, RT any way we can cancel out. So, after rearrangement combining this in the right hand side, first and third term when we combine we get ln $\frac{fi}{yi}$.

Then when you combine the second and fourth term of right hand side you will get ln P simply or ln y_i P - ln y_i = ln $\frac{yi\ P}{yi}$ and then y_i, y_i is cancelled out. So, then ln P would be there and these terms anyway are carrying Σ y_i and then Σy_i both the terms. So, that is the reason we have Σ y_i ln $\frac{fi}{yi}$ - Σ y_i ln P. Now, what is this? Σ y_i ln P is nothing but simply ln P, right?

So, Σ y_i ln P = ln P Σ y_i, Σ y_i = 1, so it is ln P that means ln $f_{mixture}$ - ln P = Σ y_i ln $\frac{fi}{yi}$ - ln P.

So, this ln P, ln P will be cancelled out from either side. Then, we have this expression ln $f_{mixture}$ = Σ y_i ln $\frac{fi}{yi}$, but this is not the final solution. However, it is important part. Now, in this equation, if you substitute Lewis fugacity rule because till obtaining this point, we have not applied Lewis fugacity rule. So, when we apply Lewis fugacity rule in this equation then what we have, we can simplify that equation further to get the required answer.

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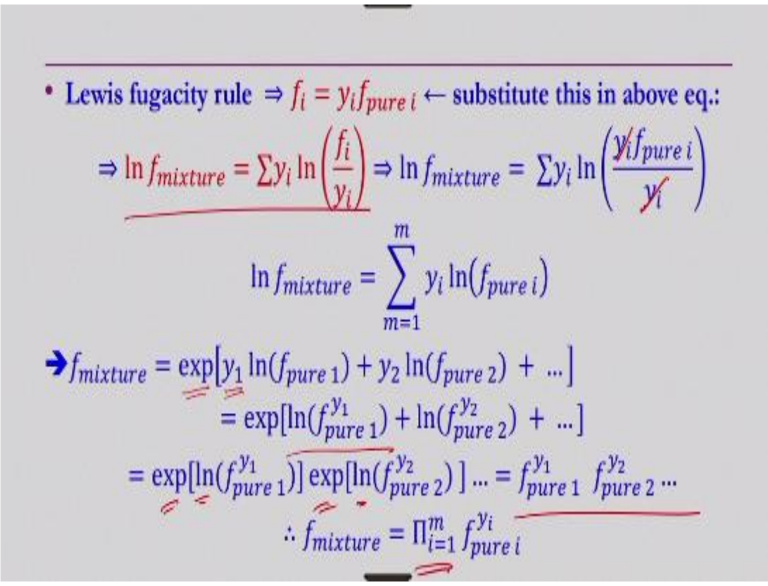

So, Lewis fugacity rule is nothing but $f_i = y_i f_{pure\ i}$ that if you substitute in this equation which we just derived, so in place of f_i, I am just writing $y_i f_{pure\ i}$. So, y_i y_i is cancelled out. So, $\ln f_{mixture} = \Sigma y_i \ln f_{pure\ i}$. This if you let us say you know first you take off the ln so that in the right hand side we get the exponential and the left hand side we have $f_{mixture}$.

So, $f_{mixture} = \exp [y_1 \ln (f_{pure\ 1}) + y_2 \ln (f_{pure\ 2}) + \ldots]$ depending on the number of components. y_i whatever is there before $\ln f_{pure\ i}$ that we take inside the ln part so that we get $\ln f_{pure\ i}^{yi}$.

So, that is $\ln f_{pure\ 1}^{y1} + \ln f_{pure\ 2}^{y2} + \ldots$, right? So now, we write this one exponential of a + b as exponential a exponential b forms, then we have this one, right? Now, so that exponential ln exponential ln for each term maybe stricken off so that we have $f_{pure\ 1}^{y1}$, $f_{pure\ 2}^{y2}$ and so on so like that, it is a product. So, that is $f_{mixture} = \Pi_{i=1}^{m} f_{pure\ i}^{yi}$ and then this product, Pi is from i equals to 1 to m because m number of components are there, hence it is proved.

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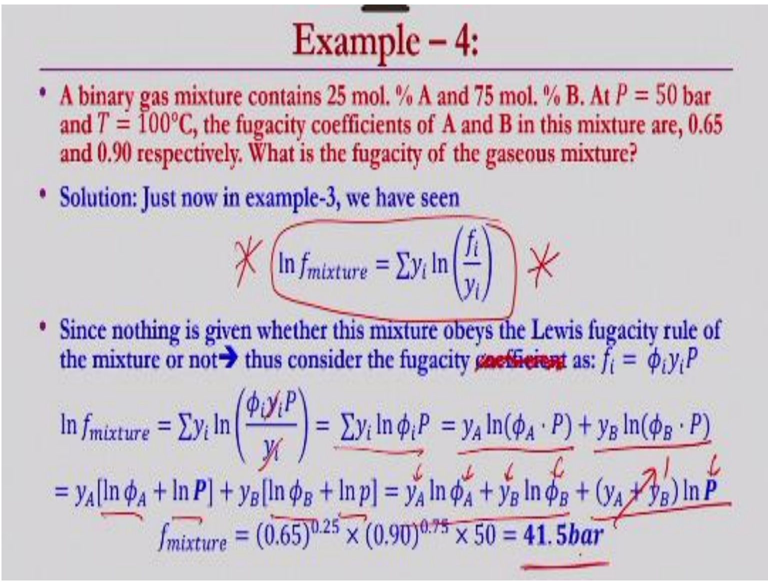

Another example problem a binary gas mixture contains 25 mol % of A and 75 mol % of B at P = 50 bar and T = 100 degrees centigrade. The fugacity coefficients that is ϕ_A and ϕ_B are given as a 0.65 and 0.9 respectively. What is the fugacity of the gaseous mixture? So, fugacity of the gaseous mixture is required that is f mixture is required, okay, but this ϕ_A, ϕ_B are given or f_A and f_B are given because P as well as the y_A, y_B are also given on mole basis, right? So individual f are given, but for the mixture we have to find out.

So, just in the previous example problem number 3, we have derived that $\ln f_{mixture} = \Sigma\, y_i \ln \frac{fi}{yi}$. So, till deriving this part, we have not made use of any assumption whether the mixture is obeying Lewis fugacity rule or not. And then now in the fourth example, it is not given whether Lewis fugacity rule is obeyed or not. So, we cannot take that Lewis fugacity rule validity as we have taken in the previous case because it is not given for this problem, it is given only for third problem.

So, in this fourth problem, up to this part derivation is same as in the previous problem. From this part onwards, the third example you know different derivation is there, but we need up to this point. So, since we have already done, I am not redoing it, okay? Now, since nothing is given whether this mixture obeys the Lewis fugacity rule of the mixture or not, thus consideration of the fugacity f_i as $\phi_i\, y_i$ P is more appropriate. So, in this equation

$\ln f_{mixture} = \Sigma\, y_i \ln \frac{fi}{yi}$, in place of f_i, I am writing $\frac{\phi i\, yi\, P}{yi}$.

So, this y_i, y_i cancelled out. So that means, $\Sigma\, y_i \ln \phi_i P$, so this I can write for a binary mixture because it is a binary mixture like this I can write it. Then what I can do, $\ln \phi_A P$, I can write $\ln \phi_A + \ln P$. Similarly, for the second one also I can write similarly like this. Now I can separate these 2 terms $y_A \ln \phi_A + y_B \ln \phi_B$ as one term and then remaining 2 terms $(y_A + y_B) \ln P$. So, this is nothing but 1.

So, when you take off the logarithmic or without taking of the logarithmic also you can substitute what is y_A given, what is y_B given, and what is ϕ_A given, what is ϕ_B is given and then P is also given. So, substitute directly and then get the $f_{mixture}$ value, okay? So, then that comes out to be 41.5 bar, okay?

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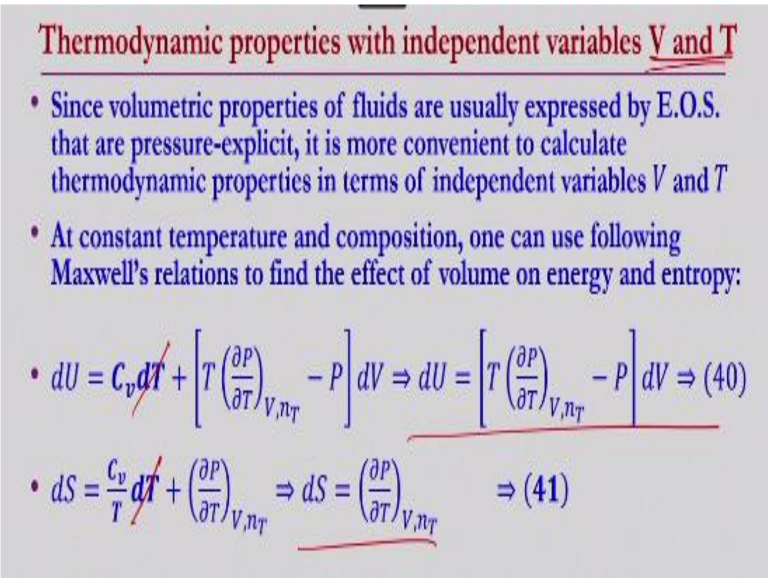

Now, what we do next? We see how to estimate thermodynamic properties with temperature and volume as independent variables because in the previous lecture we have seen, we have discussed most of the volumetric data is available as a pressure explicit rather than the volume explicit. In the previous class, we estimated thermodynamics properties from equations of state if that is available as a volume explicit form, but mostly these equations of state are available as a kind of a pressure explicit form, right? That is temperature and volume has to be independent variables, okay?

So, under such conditions, how to estimate thermodynamic properties? Again what we can start with, we can start with the Maxwell relations. From the Maxwell relations, any 2 thermodynamics properties can be estimated easily. Once 2 thermodynamics properties estimated, so the rest of the thermodynamic properties you know can be estimated, right? Since the volumetric properties of fluids are usually expressed by the equations of state that are pressure explicit, it is more convenient to calculate thermodynamic properties in terms of independent variables T and V.

At constant temperature and composition, one can use following Maxwell relations to find the effect of volume on energy and entropy. Previous lecture what we have seen? Effect of pressure on entropy and enthalpy, right? Because in the previous lecture we have written as a kind of volume explicit form, so there we can see the effect of pressure on the total entropy and enthalpy. Once the entropy and enthalpy we calculated, the rest of all other thermodynamic energies that we have calculated.

But here in this case it is a pressure explicit form. So, we are going to see effect of volume and energy and entropy that is internal energy and entropy. Once this U and s are known, h, A, G, etc., we can calculate. So, this is one of the Maxwell relations, but we are taking constant temperature. So, dU = $\left[T\left(\frac{\partial P}{\partial T}\right)_{V,nT} - P\right]dV$ that is what we are having.

Similarly, dS = $\frac{Cv}{T}$ dT + $\left(\frac{\partial P}{\partial T}\right)_{V,\,nT}$, but it is again we are doing these calculations at constant temperature and composition, so dT = 0. So, dS = $\left(\frac{\partial P}{\partial T}\right)_{V,\,nT}$. So, now if you integrate these equations, you can get the energy of the system and then entropy of the system.

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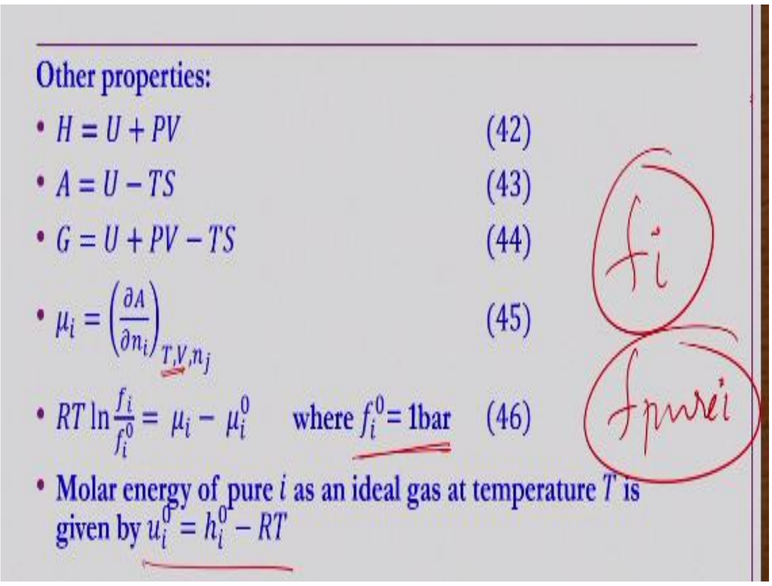

Once these two are known, rest all other things we can easily calculate as we have these several relations like H = U + PV, A = U - TS, G = U + PV - TS and then chemical potential. So, when defining chemical potential as a function of Helmholtz energy ∂A by ∂n_i T, V are kept constant along with the n_j and then this RT dln $f_i = \Delta \mu_i = \mu_i - \mu_i^\circ$ and then f_i° we are taking as a kind of reference 1 bar. Molar energy of pure i as an ideal gas at temperature T is given by

$u_i^\circ = h_i^\circ - RT$.

So, that is once you know the internal energy U and then entropy, you can calculate all these properties without any difficulty but our aim is what is this fugacity of i^{th} component in the mixture or what is the fugacity of pure component i, this is our interest, right? So, now we try to do something how to get this information as keeping temperature and volume as independent variables.

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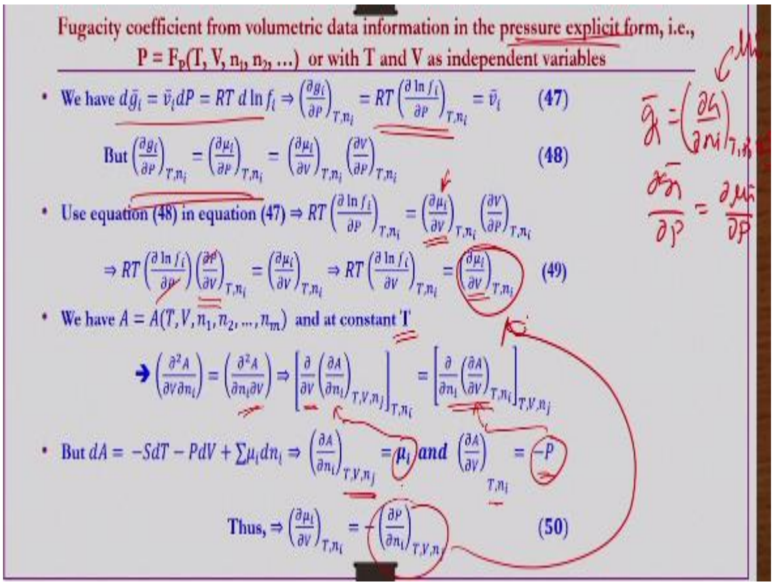

Fugacity coefficient from volumetric data information in the pressure explicit form, this is important, previous one is the volume explicit form. In the pressure explicit form that is P as function of T, V, n_1, n_2, and so on are known or as temperature and volume are independent variables, then what is the fugacity coefficient ϕ_i that is what we are doing. So, we have a relation $d\bar{g}_i$ = RT dln $f_i = \bar{v}_i$ dP this is also we have seen in one of the previous lectures, right?

So, now this equation if you partially differentiate with respect to pressure, then we get $\frac{\partial \bar{g}_i}{\partial P}$ at constant temperature and composition is nothing but $\bar{v}_i$ and that is nothing but RT $\frac{\partial \ln f_i}{\partial P}$ of at constant temperature and composition, right? So, but anyway, we do not need this third part, we need only this part okay? But what is $\bar{g}_i$? $\bar{g}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,\,n_j}$ and then what is $\left(\frac{\partial G}{\partial n_i}\right)_{T,P,\,n_j} = \mu_i$, right?

So, that means $\frac{\partial \bar{g}i}{\partial P} = \frac{\partial \mu i}{\partial P}$, so the same thing I have written like this, okay? And this $\frac{\partial \mu i}{\partial P}$, I am writing in different because now I cannot know effect of pressure because I can know effect of volume only here because temperature and volume are independent variables and out of these 2, temperature I am keeping constant, so effect of volume I can find out, but effect of pressure, I cannot find out in this case. So, then what I do? I write this one as $\left(\frac{\partial \mu i}{\partial V}\right)\left(\frac{\partial V}{\partial P}\right)$ like this, okay?

So, that means here in place of this RT $\frac{\partial \ln fi}{\partial P}$ is nothing but this particular thing, fine? By combining these 2 equations, what we get? RT$\left(\frac{\partial \ln f_i}{\partial P}\right)$ at constant temperature and composition is nothing but$\left(\frac{\partial \mu i}{\partial V}\right)\left(\frac{\partial V}{\partial P}\right)$, but our interest is f_i, okay? What is $\left(\frac{\partial V}{\partial P}\right)$ we do not know, we can find out somehow let us use and then what is μ_i? Unless we know what μ_i is, we cannot further move forward. So, that means we have to find out what is $\left(\frac{\partial \mu i}{\partial V}\right)$ now that is what we try to do right now, right?

So, before doing what we do? Whatever $\left(\frac{\partial V}{\partial P}\right)$ in the right hand side is there that I take it to the left hand side as $\left(\frac{\partial P}{\partial V}\right)$so that I can write this left hand side part as you know RT$\left(\frac{\partial \ln f_i}{\partial V}\right)$kind of thing, right? Because now I wanted to know the effect of volume on fugacity. If you change the volume, then how the fugacity is changing because you know temperature and volume are independent variables and then temperature we are fixing constant. So, now by changing V, how ϕ_i or fi is changing that we have to find out.

So, RT$\left(\frac{\partial \ln f_i}{\partial V}\right)$ =$\left(\frac{\partial \mu i}{\partial V}\right)$. So, now I have to find out this one. If I find out this one, I can substitute here, I can find out ϕ_i f_i. Once f_i is known, ϕ_i is straightforward. We have A as function of temperature, volume, and composition but at constant temperature, what can we write here? At constant temperature $\left(\frac{\partial^2 A}{\partial V \partial n_i}\right) = \left(\frac{\partial^2 A}{\partial n_i \partial V}\right)$I can write it at constant temperature. This one I can write $\left[\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}\right]_{T,\, n_i}$ = and then this part, I can write$\left[\frac{\partial}{\partial n_i}\left(\frac{\partial A}{\partial V}\right)_{T,n_i}\right]_{T,\, V,n_j}$, right?

So, now if I find what is $\left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}$ and $\left(\frac{\partial A}{\partial V}\right)_{T,n_i}$, I can substitute here and then see how I can simplify related to the chemical potential. We have equation that dA = - SdT - PdV + Σ μ_i dn_i. Now, this one at constant temperature, volume, and n_j if you partially differentiate this equation, then $\left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}$ with respect to n_i if you partially differentiate this expression by keeping temperature, volume, and moles other than n_i as constant that is n_j as constant then $\left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} = \mu_i$.

And then similarly at constant temperature and then constant composition that is what we are doing then under such conditions if you partially differentiate this equation with respect to volume then $\left(\frac{\partial A}{\partial V}\right)_{T,n_i}$ as a constant then we get that should be equals to - P from this equation, right? So, this equation also we have derived in one of the previous lectures. So, now here $\left(\frac{\partial}{\partial n_i}\right)$I can write as a kind of μ_i and then here$\left(\frac{\partial A}{\partial V}\right)_{T,n_i}$ = - P, here.

When I write it, I will get $\left(\frac{\partial \mu_i}{\partial V}\right) = -\left(\frac{\partial P}{\partial n_i}\right)$. So, I want this $\left(\frac{\partial \mu_i}{\partial V}\right)$ something in terms of measurable property so that I can easily do because I do not know any information about μ_i, okay? It is not measurable, okay? So, non-measurable μ_i is not really related to measurable pressure, the change in pressure with respect to change in the composition by keeping constant temperature, volume and n_j. So, now this I can substitute here equation number 49, okay?

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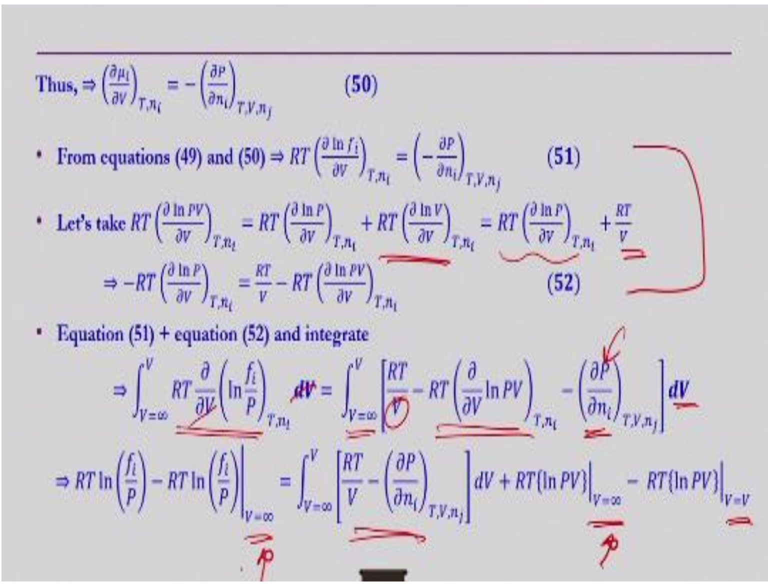

Then what we have RT$\left(\frac{\partial \ln f_i}{\partial V}\right)$ in the left hand side of the equation 49 as it is. In the right hand side what we have$\left(\frac{\partial \mu i}{\partial V}\right)$. So, in place of$\left(\frac{\partial \mu i}{\partial V}\right)$, I can write - $\left(\frac{\partial P}{\partial n_i}\right)$, right? So, let us keep this equation as it is without doing any correction but now what we do? We take RT$\left(\frac{\partial\ ln\ PV}{\partial V}\right)$ and then expanded it. If we expand it, RT$\left(\frac{\partial\ ln\ P}{\partial V}\right)$+ RT$\left(\frac{\partial\ ln\ V}{\partial V}\right)$ that I can write, right? So, this part RT$\left(\frac{\partial\ ln\ V}{\partial V}\right)$ = $\left(\frac{RT}{V}\right)$.

Why I am writing because I want something like RT$\left(\frac{f_i}{y_i P}\right)$terms or $\frac{f}{P}$ terms and then as of now there is no P term here, unless that comes into the picture. I cannot define a fugacity coefficient. I can have a relation for the fugacity, but not for the fugacity coefficient, okay? For that reason, this arrangement is there, okay? So, RT$\left(\frac{\partial\ ln\ PV}{\partial V}\right)$is nothing but simply RT$\left(\frac{\partial\ ln\ P}{\partial V}\right)$+ RT$\left(\frac{\partial\ ln\ V}{\partial V}\right)$. Now, what I do? I write this part - RT, this part whatever first term in the right hand side that I take to the left hand side, so that is - RT$\left(\frac{\partial\ ln\ P}{\partial V}\right)$and then right hand side term $\frac{RT}{V}$ is as it is.

This remaining term - RT$\left(\frac{\partial\ ln\ PV}{\partial V}\right)$that I have written in the right hand side of the equation number 52. Now, simply add these 2 equations, 51 and 52. Then, you will have this RT $\frac{\partial}{\partial V}$ (ln f_i) - RT$\frac{\partial}{\partial V}$ (ln P). I can write RT $\frac{\partial}{\partial V}\left(\ln \frac{f_i}{P}\right)$, ln A - ln B = ln $\frac{A}{B}$ form and then we are integrating, okay? That is left hand side is done. Right hand side what are the terms are we having? We are having $\frac{RT}{V}$ - RT $\left(\frac{\partial}{\partial V} \ln PV\right)$ - $\left(\frac{\partial P}{\partial n_i}\right)$terms we are integrating.

Now, coming to the integration limits, we are taking V = infinity to certain V value, right? Why is it? Because we cannot start with 0, V = 0 because any system that you take, it will have some volume, so 0 volume that means system is not existing that we cannot, right? But the other side if you see V = infinity in the sense it is a large volume, infinite volume, and then particles if the volume is infinite then fluid particles or whatever the gas particles are there, they will be away from each other.

Then under such conditions if V tends to infinity that gas is obviously ideal gas behavior kind of thing. So, from ideal gas behavior this V is equal to infinity will serve two purpose as a kind of lower limit of the integration and then as V decreases, the non-ideality will come into the picture. So, that other limit V will be taken as a kind of upper limit. So, either way it is applicable as a kind of lower limit of the integration as well as to bring the reference.

Because all these calculations wherever the corrected pressure, the fugacity, etc. that we started defining by taking the kind of ideal gas as a kind of reference from the Gibb's Duhem equation we have taken you know whatever the constant temperature and then pressure, μ_i is nothing but you know that SdT - PdV + Σ μ_i dn_i = 0. In that case, we have taken from there by taking constant temperature and pressure, I defined you know this $\frac{\partial \mu i}{\partial n_i}$ = G kind of thing, those kind of things we have done and then we brought it that is basically the corrected pressure concept.

The fugacity is nothing but corrected pressure concept, right? That concept has evolved from the limitation of ideal gas, right? If the gas is obeying the ideal behavior, then fugacity of the mixture should be equal to the total pressure that is one limitation and then let us say if it is a mixture of the gases and then for the fugacity of the i^{th} component in the mixture should be equal to the partial pressure of that component in the ideal gas mixture that is the basis limiting condition that we have taken that is the reason we have to take this V infinity as a kind of reference, right?

In the previous case where we have written volume explicit form derivations, there we have taken P = 0 as a kind of a lower limit why because there also when P = 0 or P tends to 0 we can say that system reduces to the ideal gas behavior, right? So, that is the reason here we have taken the limits V infinity to V, not from 0 to V, okay? Now when you simply integrate this one RT ln $\frac{f_i}{P}$, we will get here, okay? Because this dV dV is cancelled and then $\frac{f_i}{P}$ at certain volume we do not know, so we are estimating it, okay?

We are developing an expression that is as it is and then lower limit is RT ln ln $\frac{f_i}{P}$ at V is equal to infinity. At V = infinity, what is $\frac{f_i}{P}$ that we have to find out, okay? And now here what is V, we do not know. What is $\frac{\partial P}{\partial n_i}$, we do not know. So, we cannot integrate these 2 terms. So, then what we write? We write integral V = $\int_{V=\infty}^{V} \left[\frac{RT}{V} - \left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}\right]$ as it is and then this part if you integrate, you will get RT ln PV, simply RT ln PV because $\left(\frac{\partial}{\partial V}\ln PV\right)$ and then dV with respect to dV we are doing integration.

So, that is dln PV. So, integral of dln PV simply ln PV. So, there are 2 limits. One is the RT ln PV at V = V, another one is RT ln PV at V = ∞. So, there is a - symbol here. So, the lower limit is getting a + symbol here and the upper limit is getting a - symbol here. Now, we have to find out what is ln PV at V = ∞, this also we have to find out and then what is ln $\frac{f_i}{P}$ at V = ∞ that also we have to find out, then it is straightforward.

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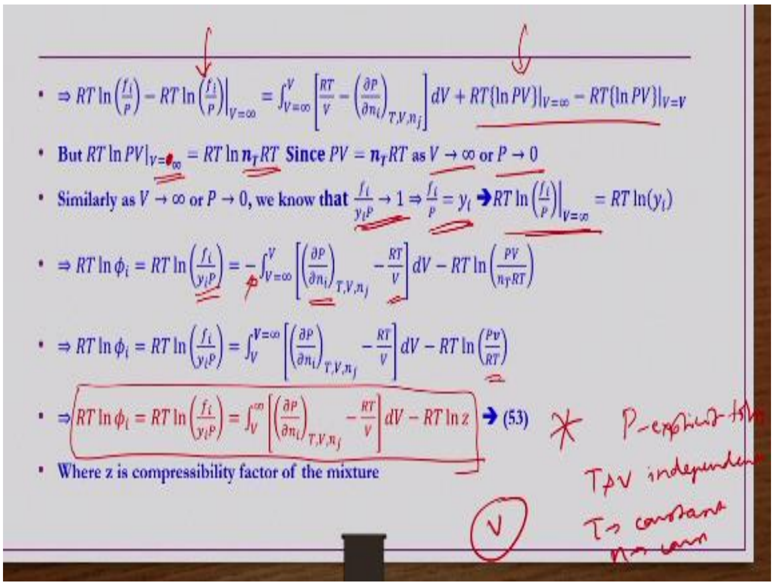

So, the same equation I have written here once again. Now RT ln PV at V = ∞. At V = ∞ means what, it is ideal gas behavior. For the ideal gases, P V is nothing but nRT. So, that I can write as RT ln n_TRT because as V tends to ∞ P V is nothing but n_TRT that is ideal gas obvious, one thing is clear. Then as V tends to ∞, we know that it is ideal gas behavior, so far the ideal gas behavior we know that the fugacity coefficient has to be 1 that is $\frac{f_i}{y_i P} = 1$.

That means at V tends to ∞ or P tends to 0, $\frac{f_i}{P}$ = y_i because at V tends to infinity or P tends to 0, the system reduces to the ideal gas behavior and then for ideal gas behavior fugacity coefficient is 1, so that is $\frac{f_i}{y_i P}$ = 1 that means $\frac{f_i}{P}$ = y_i. So that is RT ln $\frac{f_i}{P}$ at V = ∞ = RT ln y_i. So, here we can substitute ln y_i and then here we can substitute ln n_TRT, then what we have?

Here RT ln $\frac{f_i}{y_i P}$ we will get left hand side, so that is RT ln ϕ_i and then right hand side, I am just writing $\frac{\partial P}{\partial n_i}$ as a first term - $\frac{RT}{V}$ as a second term so that is the reason this - is coming here, and then these 2 terms if you substitute here n_TRT, then we can write RT ln $\frac{PV}{n_T RT}$. So, this $\frac{PV}{n_T RT}$ = $\frac{Pv}{RT}$ = z, okay? Now this here, here what I am doing in order to remove this - symbol integration limits I am changing certain V to V = ∞, the lower and upper limit, I am reversing, right?

So, then that - is gone, okay? This is PV by RT. So, that means I can have in place of PV by RT ln z, z is nothing but compressibility factor of the mixture. So that means

RT ln ϕ_i = RT ln $\frac{f_i}{y_i P}$ = $\int_V^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right]dV$ - RT ln z is the expression for so called fugacity coefficient of that particular component in the mixture, right? And then here we have pressure explicit form and then T and V independent variables, out of these two, T we are keeping the constant and then n components in the composition also constant we are keeping.

That means effect of V can find out if there is a change in V, how this v_i is changing that is what we can get by now simply integrating this equation and simplifying it. So, z is the compressibility factor of the mixture.

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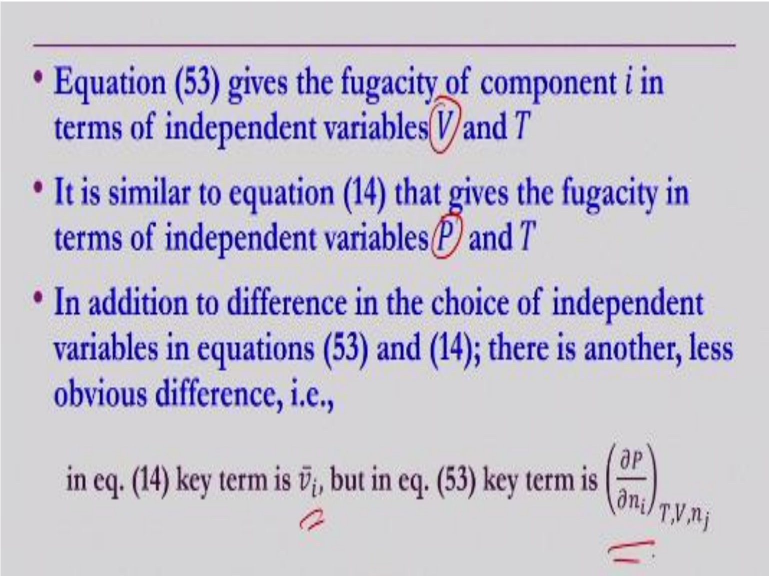

So, equation 53 gives the fugacity of component i in terms of independent variables V and T, whereas equation 14 that we derived in a previous lecture that gives the fugacity in terms of independent variables P and T. Here, the effect of volume we can find out, in the previous one we can find out effect of pressure on fugacity at constant temperature and composition, right?

So, in the previous one, we have a $\bar{v}_i$, here we have $\left(\frac{\partial P}{\partial n_i}\right)$, $\bar{v}_i$ is partial molar volume, but $\left(\frac{\partial P}{\partial n_i}\right)$ is not partial pressure. So, how to get this fugacity of the pure component i if the equation of state is available in a pressure explicit form. So, that part we will see now.

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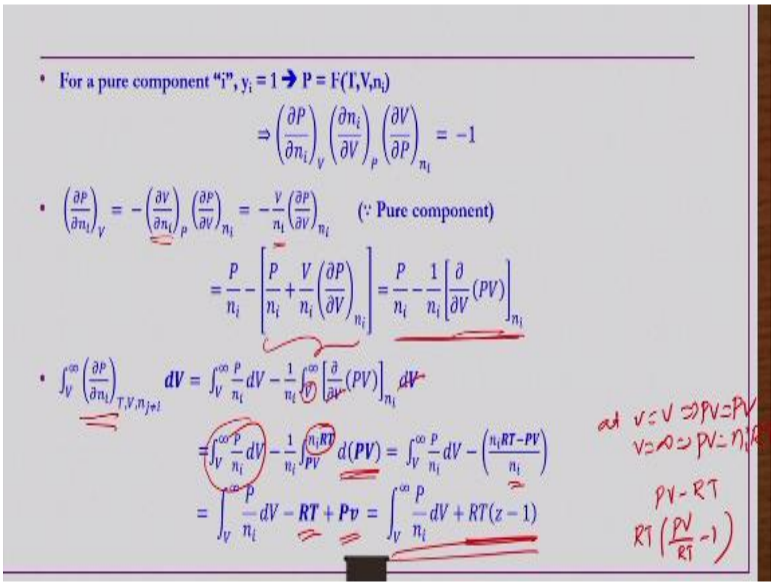

For a pure competent i, $y_i = 1$ and $n_i = n_T$ because there is only one single component, pure component in a pure form. So, then equation of state will be having the form P as a function of temperature, volume, and n_i number of the pure component i. Then, we know that $\left(\frac{\partial P}{\partial n_i}\right)_V \left(\frac{\partial n_i}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_{n_i} = -1$ from the principles of differentiation. Then, this we can write $\left(\frac{\partial P}{\partial n_i}\right)_V = -\left(\frac{\partial V}{\partial n_i}\right)_P \left(\frac{\partial P}{\partial V}\right)_{n_i}$, this is what we can know.

Then for pure component we know that this $\left(\frac{\partial V}{\partial n_i}\right)_P = \frac{V}{n_i}$ that is molar volume itself that is partial molar volume is equal to the molar volume of that pure component because the component is pure. Then molar volume we can write it as total volume by the number of moles that is $\frac{V}{n_i}$ and then here in this case now, $\left(\frac{\partial P}{\partial n_i}\right)_V = -\frac{V}{n_i}\left(\frac{\partial P}{\partial V}\right)_{n_i}$. Now, what we do?

We add and then subtract $\frac{P}{n_i}$ from this expression and then we rearrange this part $\frac{P}{n_i} + \frac{V}{n_i}\left(\frac{\partial P}{\partial V}\right)_{n_i}$ that we can write it as $\frac{\partial}{\partial V}(PV)$. This is what we can write, right? Then, we need actually $\left(\frac{\partial P}{\partial n_i}\right)_V$ in fugacity expression and integral of $\left(\frac{\partial P}{\partial n_i}\right)_V$ we need. So that now we try to do. So $\left(\frac{\partial P}{\partial n_i}\right)_V$ here we have seen it for pure component is nothing but $\frac{P}{n_i}$ - $\frac{1}{n_i}\frac{\partial}{\partial V}(PV)$, okay? So, if you integrate this part $\int_V^\infty \frac{P}{n_i}\, dV - \frac{1}{n_i}\int_V^\infty \left[\frac{\partial}{\partial V}(PV)\right]_{n_i} dV$.

So, now here this dV dV if you cancel out, then we can have an integral of dPV, integral of dPV is nothing but PV and then at V = V, we will be having PV = PV itself as a lower limit because now limits also we have to change here, in the previous case it was with respect to change in volume, so lower limit was V. Now it is with respect to PV. So, when V = V, then PV should be PV and then when V = infinity, then PV should be same as, you know, ideal gas behavior that is n_iRT or n_TRT, so that is what we have written.

So, upper limit will become n_iRT here in this case if you are doing integration with respect to PV, okay? So, then when you integrate this part, we will be having PV and then upper limit n_iRT and lower limit PV. So, n_iRT - PV and then this divided by n_i is as it is, whereas the other part, this part we cannot do the integration because what is that P we do not know, we are developing a kind of generalized expression, okay? So, now integral $\left(\frac{\partial P}{\partial n_i}\right)_V$ we are having it as $\int_V^\infty \frac{P}{n_i} dV$ - n_iRT - $\frac{PV}{n_i}$, right?

So, now here, we know if I write this one - RT + Pv we will be getting because $\frac{V}{n_i}$ is nothing but molar volume, so + Pv. So, Pv - RT = RT (z – 1). So, Pv - RT, if you take RT as common, then we have $\frac{Pv}{RT}$ - 1. So, $\frac{Pv}{RT}$ = z, so that is RT (z - 1). So, this expression we will be substituting in place of integral $\left(\frac{\partial P}{\partial n_i}\right)_V$ in equation number 53 that we have derived.

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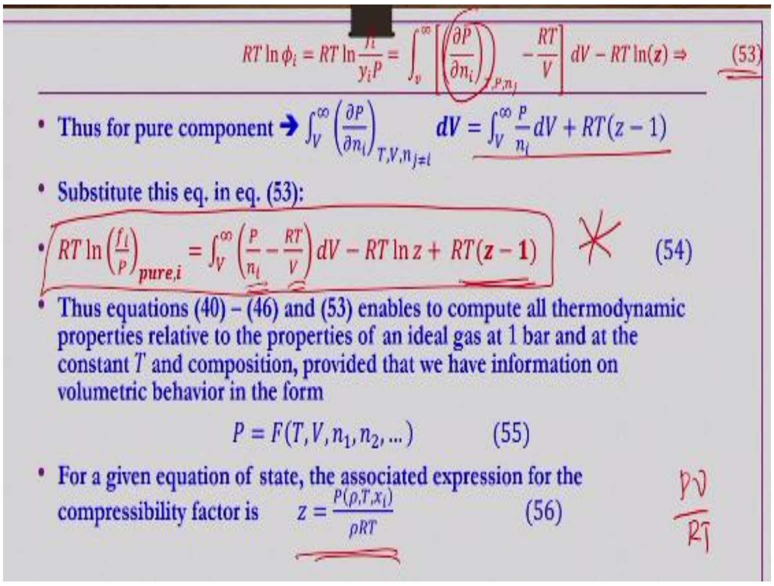

So, equation number 53 is this one. So, in place of $\left(\frac{\partial P}{\partial n_i}\right)_V$, we will be writing $\int_V^\infty \frac{P}{n_i} dV + RT(z - 1)$ that is what we are going to write. So, that is nothing but this one, in place of integral $\left(\frac{\partial P}{\partial n_i}\right)_V$ dV, we will be writing $\int_V^\infty \frac{P}{n_i} dV + RT(z - 1)$. Then, we will be having this expression. So, $\int_V^\infty \frac{P}{n_i}$ and then integral $\frac{RT}{V}$ we are writing together whereas RT (z - 1) we have written separately because it is not under integration. So, this is the expression for a fugacity of pure component i if the equation of state is available in a pressure explicit form, okay?

So, if the equation of state is available as a kind of pressure explicit form for a pure component i, then if you wanted to measure the fugacity of that pure component i, you have to use this expression. So, now, what we understood from equations 40 to 46 and 53 will enable us to estimate all thermodynamic properties related to the properties of ideal gas at 1 bar and at constant temperature and composition provided that we have information on volumetric behavior in the form of pressure explicit form like P is function of temperature, volume, and composition as given here, right?

For a given equation of state the associated expression for the compressibility factor $\frac{PV}{RT}$ can also be written as $\frac{P}{\rho RT}$ as well, so that is we are writing here, okay?

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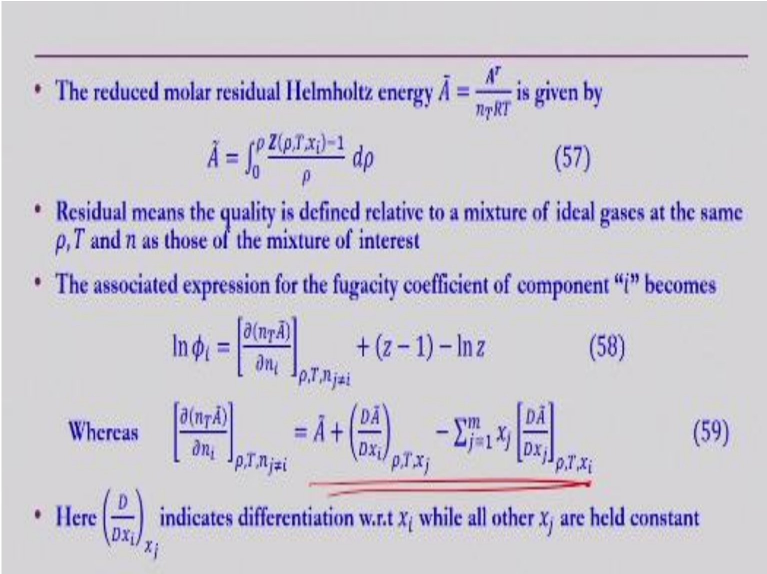

Now, if someone wanted to write an expression for fugacity in terms of Helmholtz energy, then reduced molar residual Helmholtz energy Ã can be written as A^r, A^r stands for reduced Helmholtz energy. Reduced Helmholtz energy is nothing but the Helmholtz energy at the realistic conditions - Helmholtz energy at the ideal conditions, okay? So, then Ã can be written in terms of compressibility factor as $\int_0^{\rho} \frac{Z-1}{\rho} d\rho$.

Residual means the quality is defined related to a mixture of ideal gases at the same ρ, T and n as those of mixture of the interest. So, then associate expression for the fugacity coefficient of component i becomes $\ln \phi_i = \left[\frac{\partial(n_T\tilde{A})}{\partial n_i}\right]_{\rho,T,n_{j\neq i}} + (z-1) - \ln z$. Actually, this expression is nothing but the same thing whatever we have seen in equation number 53, but only thing that in place of this one, we will be getting integral $\left(\frac{\partial P}{\partial n_i}\right)_V - \frac{RT}{V} dV$, this is what we will get if you simplify this expression back in terms of measurable property like pressure, volume, temperature, etc., okay?

But anyway we are not doing that one because we need one expression that we already have, so that is more useful and explicit because it is in measurable pressure, temperature, volume, and composition form. Here in this expression, $\left[\frac{\partial(n_T\tilde{A})}{\partial n_i}\right]_{\rho,T,n_{j\neq i}}$ is given by this expression, whereas $\frac{D}{Dx_i}$ is nothing but a differentiation with respect to x_i while keeping all other x_j as constant, okay?

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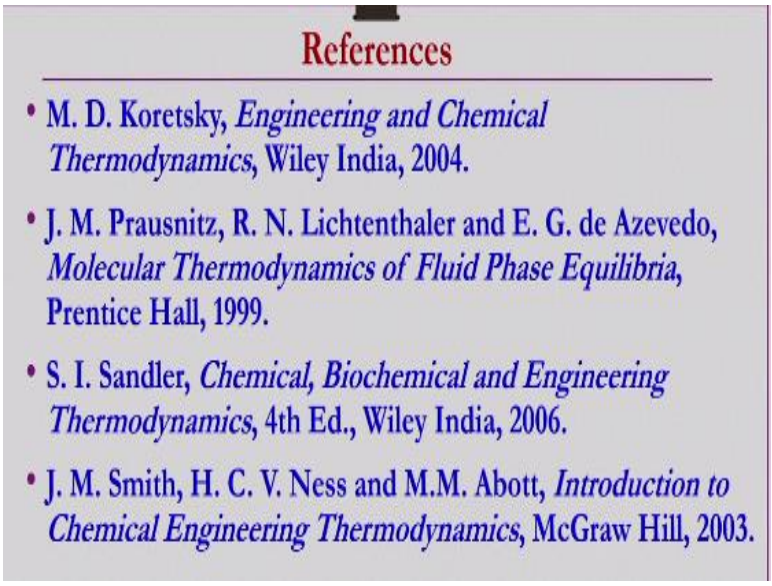

The references for this lecture are given here. Engineering and Chemical Thermodynamics by Koretsky. Molecular Thermodynamics of Fluid Phase Equilibria by Prausnitz et al. Chemical, Biochemical, and Engineering Thermodynamics by Sandler. Introduction to Chemical Engineering Thermodynamics by Smith et al.

Thank you.