Lecture – 4
Thermodynamic Properties from Volumetric Data

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is Thermodynamic Properties from Volumetric Data. Before going into the details of how to estimate the thermodynamic properties from volumetric data, what we do? We have a kind of recapitulation of what we have seen in last couple of lectures.

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We have seen like you know distribution of component i between 2 co-existing phases alpha and beta at equilibrium. So, under such conditions let us say one particular component i has been distributed between two or more co-existing phases, those phases are at equilibrium. So, then how this component i is being distributed in all co-existing phases? Those calculations, we aim to see. So for that conditions for that reason, what we have seen? We have seen that you know chemical potential of that particular component has to be equal in all co-existing phases at equilibrium that is what we have seen, right?

So, then according to that one what we have seen? We have also derived this chemical potential of that particular component i has to be equally in all co-existing phases at equilibrium, that derivation also we have done. That is, let us say if we have taken only 2 phases $\mu_i^\alpha = \mu_i^\beta$, this is what we have derived, right? So, now, this is actually chemical potential and then it is a very

thermodynamics abstract mathematical kind of variable which is not having any direct relation to the real life measurable properties such as temperature, pressure, composition, etc.

Then what we have to do? We have to do some kind of you know arrangement so that we can make this chemical potential to be related to temperature, pressure, and composition of that particular component in that particular phase, right? If you have more than 2 phases, for all those phases, we have to make relation between the chemical potential of that particular component in each phase to the temperature, pressure, and composition of all the components in that particular phase.

Those things we have to do that is we have also related μ_i^α to temperature, pressure, then x_1^α, x_2^α, etc. Similarly, we have also related that μ_i^β to temperature, pressure, x_1^β, x_2^β, etc. Actually we have not directly made a kind of relation, but we thought of that we have to make this kind of relation, right? So, this conclusion when we came to this point, so we were clueless how to make a kind of connection between this chemical potential and temperature, pressure, and then composition for each phase.

So, then what we thought of? We thought of establishing these relations, in order to establish these relations, we introduced some auxiliary functions such as fugacity and activity, right? And this fugacity and activity are much closer to physical sense than chemical potential as we have seen that fugacity can be related or can be referred as a kind of corrected pressure, right? If it is ideal gas, then fugacity = the total pressure of the system.

If it is a mixture of ideal gas, then fugacity of component i = the partial pressure of that particular component in the ideal gas mixture. Those kinds of relation that we have made between fugacity and then real life measurable variables such as here in this case pressure. So, those kinds of things we have seen. So, that is what we define this auxiliary functions fugacity and activity and what we have seen this fugacity is much closer to the physical sense than the chemical potential.

Chemical potential how to relate to the temperature, pressure, composition, we are not having any idea, but then we introduce some auxiliary functions like fugacity and activity coefficient, then we realized that you know we can make a relation between these auxiliary function to the

temperature, pressure, and composition that is what we realized, right? The concept of this fugacity and activity are coming from the ideal behavior, okay? So, this is also we have seen.

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- Say α is vapour; β is liquid $\Rightarrow$ $\boxed{\phi_i y_i P = \gamma_i x_i f_i^\circ}$ $\Leftarrow$ $\mu_i^\alpha = \mu_i^\beta$

  where ϕ_i – fugacity coefficient

  γ_i – activity coefficient

  f_i° – fugacity of component i at some fixed condition known as standard state

- This (above) transformation comes from the concept of ideal behaviour of the system

Let us say if we have 2 phases alpha and beta phase and if you take alpha phase as vapor phase and beta phase as a liquid phase, then $\mu_i^\alpha = \mu_i^\beta$ we can write it as $\phi_i\, y_i\, P = \gamma_i\, x_i\, f_i^\circ$. This is also we have seen in the previous lecture. Here, ϕ_i is nothing but the fugacity coefficient and then γ_i is nothing but the activity coefficient, f_i° is nothing but fugacity of component i at some fixed condition such as standard states.

In general it is taken as a kind of saturation pressure f_i° for majority of the cases, but however, it depends on what reference state that we have taken. So, those things we again get into the details when we discuss about the liquid mixtures. And then this transformation, whatever transformation from the chemical potential to the activity coefficient or fugacity coefficient like this are shown here in this equation that is coming from the concept of the ideal behavior of the system.

As I said, if you take a kind of pure gas, then fugacity of that particular gas is equals to the total pressure of the system provided the gas is ideal gas, okay? And then if you have a kind of mixture of gases and then that mixture is obeying the ideal behavior then fugacity of any component i = the partial pressure of that particular component that is the basis that we have taken in order to get this transformation, okay?

So, that we can have a kind of transformation from the chemical potentials to these auxiliary functions and then also simultaneously we have the relation between these auxiliary functions and temperature, pressure, and composition on the system, okay?

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Now, for mixture of ideal gases $\phi_i = 1$, fugacity is equals to the total pressure for the pure gas if the gas is ideal gas. If it is mixture of ideal gases, then fugacity of any component i is equals to the partial pressure, but fugacity coefficient is equals to 1, okay? So, that means if ideal behavior is there, so then this fugacity coefficient should be 1. Similarly, if you have ideal liquid mixtures at low pressure, then activity coefficient $\gamma_i = 1$. That means at the ideal condition both of these things are equal to 1 that is what the limitation of these fugacity and activity coefficient that we have, okay?

The f_i° is given by saturation pressure of pure liquid i at temperature of interest and these auxiliary functions are numerical factors of the order of unity that establish the correlation between the real mixtures and those by ideal mixture. So, let us say if $\phi_i = 1$ then we can say that it is a kind of ideal gas mixture. If it is more than 1 then we can say that there is a kind of you know non-ideality is there and then how much is non-ideality that depends on the magnitude of this ϕ_i that we are going to measure, okay?

So, this ϕ_i and then γ_i are going to give a kind of information how much are they away from the ideal behavior, okay? If they are equal to 1 then we can say that the both vapor and then liquid phases are in a kind of ideal behavior, they are obeying ideal behavior. If they are not equal to 1, then we can say there is non-ideality and depending on the magnitude of the ϕ_i and

γ_i we can say how much non-ideality is there? How strong is the non-ideality in the given vapor or liquid phase respectively, depending on the ϕ_i and then γ_i values?

Now, in reality, for most cases we cannot assume ideal behavior obviously and must establish following 2 relations that is ϕ_i = function of temperature, pressure, y_1, y_2, some function F_ϕ and then similarly γ_i function of temperature, pressure, x_1, x_2, that is composition, some function F_γ. So, what are these functions? Unless if you know these functions, you cannot solve this problem, let us say 2 phase whatever that information we have $y_i\ \phi_i\ P = x_i\ \gamma_i\ f_i^\circ$ if you want to solve this equation for non-ideal system.

Actually for non-ideal system, we should know this ϕ i and then γ, then only we can solve this problem and then only we can solve this equation and then get what is x_i and y_i that is how this i^{th} component is being distributed between these 2 phases at equilibrium that you can calculate only when you know what is this ϕ_i and what is this γ_i, right? And then we understand these are functions of temperature, pressure and then composition.

So, the aim of this particular lecture and then coming 2 lectures is nothing but establishing some kind of relations for this fugacity coefficient. Later on, we will be having information on how to establish this relation between activity coefficient and then temperature, pressure, and composition but next few lectures will be concentrating on this particular lecture, okay? Now, already as we are saying that $\phi_i = 1$ for ideal gases or ideal gas mixtures then you know when we use $PV = RT$ and then calculate the fugacity coefficient then we will get 1.

So, if the mixture is not the kind of ideal mixture but it is a real mixture having some non-ideality, so then how to get this ϕ_i information? That is what the aim of this particular lecture and that information we can get if you know information about the volumetric data of the system. Volumetric data in the sense some information about the PVT information like pressure, function of temperature, volume and composition or you know volume function of temperature, pressure, and composition such kind of information.

If we have that information we can use in order to get this fugacity coefficient and there are a few relations. Those relations that we are going to derive now and then we take a kind of example cases. Let us say Van der Waals gas mixture which is obeying Van der Waals equation of state which is displaying some amount of non-ideality at moderate pressure. So, for that Van

der Waals equation at moderate pressure, what is the fugacity coefficient for the mixture of gases as well as for the case of a pure gas obeying this Van der Waals equation? That is what we are going to do in this particular lecture.

So, in order to get this function ϕ_i as function of temperature, pressure, composition, we need to have a kind of a volumetric data information, okay?

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So, thermodynamic properties from volumetric data. Most thermodynamic properties of interest of any substance regardless of whether it is pure or a mixture in a phase equilibrium can be calculated from thermal and volumetric measurements. Thermal measurements in general that is about the heat capacities give information as how some thermodynamic properties vary with temperature, whereas the volumetric measurements give information on how thermodynamics properties change with pressure or density at constant temperature, okay?

That is, if you have information this V as a function of temperature, pressure, and composition or if you have this function P as function of temperature, volume, and composition, then we can make use of either of this information and then we can find out any thermodynamic properties. First we can make use of Maxwell's relations to get you know this internal energy or enthalpy, etc. Once you know any 2 properties, rest all other thermodynamic properties you can easily find out.

But our interest is not finding out thermodynamics properties from volumetric information, but making use these equations to get information about fugacity coefficient of a component i in

the mixture, okay? So, we are going to derive relations for this ϕ_i if you know either this function or this function, actually they are the same, but what is the difference here you know independent variables are temperature, pressure, and composition, in the case here temperature, volume and composition. So, what we do?

One case we take at constant temperature and composition and another case at constant temperature and composition again, we derive relations for ϕ_i as T and P as independent variables and in other case we obtain relation for the same ϕ_i as T and V as independent variables. These relations we are going to derive.

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So, let us say if we have independent variables T and P, then using the Maxwell's relations, one can obtain the effect of pressure on enthalpy and entropy at constant temperature and composition using these 2 relations $dH = C_p dT + V - T \left(\frac{\partial V}{\partial T}\right)_{P,\ nT} dP$. Since, we are doing all these things at constant temperature and composition, this condition must be remembered, whatever the fugacity relations that we are going to derive, they are valid at constant temperature and composition.

So, since the temperature is constant then $dT = 0$. So $dH = V - T \left(\frac{\partial V}{\partial T}\right)_{P,\ nT} dP$. Using this relation if you integrate this relation, you can get the information about enthalpy and then how this enthalpy is changing by changing in pressure or the effect of pressure on this enthalpy we can find out by integrating this equation. Similarly, $dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_{P,\ nT} dP$, this is another

Maxwell relation. These 2 are Maxwell's relations only, right? Since it is constant temperature, again dT = 0.

So, dS = - $\left(\frac{\partial V}{\partial T}\right)$ P, nT dP, right? So, also if you integrate this equation, you can obtain the entropy as function of pressure or with the change in pressure how the entropy is changing that you can find out by integrating this equation number 2. Once you have H and S, then you can calculate other energies like U = H - PV, now H is already known, so - PV if you do, you get the U. Then A = H - PV - TS or U - TS and then G = H - TS and then $\mu_i = \left(\frac{\partial G}{\partial ni}\right)$ T, P, nj.

So, all this once you know H and S, then you can calculate U, A, G, these energies also you can calculate. Once Gibb's energy G is known.

Then you can find out the chemical potential, $\mu_i = \left(\frac{\partial G}{\partial ni}\right)$ T, P, nj as a kind of definition that we can take for the chemical potential evaluation, right? Because we know that once we know the chemical potential.

You know $\mu_i - \mu_i° = RT$ dln f_i this we know it, right? So, you know the G, so then you know the μ_i chemical potential.

So, chemical potential at required temperature and then at reference temperature and pressure, these conditions if you get, so difference you do, then that difference whatever is there that can be related to the fugacity coefficient of that particular component in a mixture. So, that is the reason you know we can get required information for fugacity and then followed by fugacity coefficient $\phi_i = \frac{fi}{yi\ P}$ this thing we can calculate, okay?

This RT dln f_i that we can write RT ln $\frac{fi}{fi°} = \mu_i - \mu_i°$, $f_i°$ is the fugacity of that particular component at some standard reference state, which one are we taking as reference state that also makes difference.

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So, some of the symbols that we may be using in this and then coming lectures are $h_i°$ is nothing but molar enthalpy of pure i as an ideal gas but at temperature T, $s_i°$ is molar entropy of pure i as an ideal gas at temperature T and 1 bar pressure. Then, $\mu_i° = h_i° - Ts_i°$, i is pure i and then $f_i°$ we are taking 1 bar as a kind of reference with respect to the ideal gas behavior, okay? The n_i is nothing but number of moles of i, n_T is nothing but total number of moles that are present in the system, y_i is nothing but mole fraction of i which is nothing but n_i by n_T, okay?

Total properties are you know represented by the capital letters and then whatever the extension properties on molar basis are there they are you know represented by these smaller letters like u, v, h, etc. If we have bar, then that bar to the smaller letters that indicates in partial molar properties, okay?

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So, now, the most important thing how to obtain the fugacity coefficient from volumetric data information in the volume explicit form that is you know whatever the volumetric information is there that is given as a kind of this form volume is function of some temperature, pressure and then composition of this system, okay? That is known as the volume explicit form or temperature, pressure as independent variables right, okay? So, then under such conditions, how to obtain this fugacity coefficient that we will be seeing first.

We have this Gibb's Duhem equation $SdT - VdP + \Sigma\, n_i\, d\mu_i = 0$. Now, this one if you write for partial molar case, partial molar properties, that is partially differentiate this equation with respect to n_i by taking temperature, pressure, and μ_i are as independent variables, then what we will get? Obviously we will get $\bar{s}_i\, dT - \bar{v}_i\, dP + d\mu_i\, (1) = 0$. That means $d\mu_i = \bar{v}_i\, dP - \bar{s}_i\, dT$, right? Now, this relation is coming from the Gibb's Duhem equation.

It is very much essentially important especially in terms of you know obtaining the fugacity coefficient because this relation gives the change in chemical potential of that particular component change with respect to changes in temperature and pressure as independent variable, right. But in our case what we are taking T constant, all these derivations whatever we are doing, here temperature is constant and then composition is also constant, number of moles of the system are remaining constant.

So, obviously, the second term of this equation is gone. So, then we will be having $\left(\frac{\partial \mu i}{\partial P}\right)_T = \bar{v}_i$ $= d\mu_i = \bar{v}_i\, dP$ and then we are already having a relation for $d\mu_i$ as nothing but RT dln f_i. So, that

is $d\mu_i$ is nothing but RT dln f_i by definition, this is what we are having, right? Now if you combine these 2 equations, what you can get dln $f_i = \frac{\bar{v}i}{RT}$ dP that means this equation is so important that if you know what is this $\bar{v}_i$ with respect to change in pressure, then you can know what is the change in fugacity of that particular component.

So, this is what we want, but in order to solve this equation, you should know what is $\bar{v}_i$ and this $\bar{v}_i$ you can get only if you have this V as function of temperature, pressure, and composition, okay? So, let us further go into the details of this derivation. So, but $\phi_i = \frac{fi}{yi\ P}$ and then$\frac{fi}{pi}$, I can write y_i P is nothing but you know partial pressure for the system, okay? So now what we can write, $f_i = \phi_i\ y_i\ P = \phi_i\ p_i$, this is what we can write, but we want ln f_i or dln f_i.

So, in place of dln f_i we can write dln ϕ_i + dln p_i because fi = ϕ_i * p_i and then right hand side $\frac{\bar{v}i}{RT}$ dP as it is, right? So, now this equation we can make use when we have this information partial pressure. So, but what we try to do? We try to have an expression purely as a function of temperature, pressure, and composition and nothing else. So, we try to get over of this one also. So for that, what we do?

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We know p_i is nothing but y_i P that means we can write ln p_i = ln y_i + lnP that we can write, right? But if you take dln p_i, then we have dln y_i + dln P and all in these calculations, repeatedly I am mentioning these calculations are for the constant temperature and composition case. If the composition is constant, so then dln y_i = 0 that means for constant y_i, dln p_i = dlnP, right?

So, now in the equation number 12 wherever we have dln p_i, in that place if you write a dln P and then simplify this equation, we have this equation dln ϕ_i + dln P = $\frac{\overline{v_i}}{RT}$ dP.

So, whatever the dln P is there that I can take to the right hand side of the equation so that I can have dln ϕ_i = $\overline{v_i}$ by RT dP - dln P that I can write $\frac{\overline{v_i}}{RT}$ - $\frac{1}{P}$ dP, right? Now, we have a more explicit kind of equation, only thing that you need to know what is the pressure, total pressure of the system at what constant temperature are you calculating fugacity coefficient that you wanted to know and then $\overline{v_i}$ that is you know partial molar volume you need to know that you can know from the volumetric data, okay?

So, now we have a direct relation between fugacity coefficient of component i to measurable properties such as temperature, pressure, and composition, okay? So, now let us integrate this equation. So, then we have after integrating you know we get this equation integral $\int_1^{\phi i}$ dln ϕi And then right hand side dP is changing from 0 to P when P = 0 then ϕ_i = 1. If P = 0 or P tends to 0 that means it is ideal behavior and for ideal behavior case fugacity coefficient is 1.

So, those are the lower limits of 2 cases, at some pressure P, what is ϕ_i that we do not know that is what we are calculating. So, when you substitute these limits, then you have

ln ϕ_i $_=$ $\int_0^P \left(\frac{\overline{v_i}}{RT} - \frac{1}{P} \right)$ dP, right? The same equation if I multiply both sides by RT, then I can have RT ln ϕ_i = RT ln $\frac{f_i}{y_i P}$ because ϕ_i is nothing but simply $\frac{f_i}{y_i P}$ = $\int_0^P \left(\overline{v_i} - \frac{RT}{P} \right)$dP. This is the equation that we need.

So, now you can see we have a kind of explicit equation between fugacity coefficient of component i in the mixture to the temperature, pressure and composition of the system, right? If you wanted to know the fugacity coefficient of any component i in the system, only thing that you wanted to know is $\overline{v_i}$ and at what temperature and pressure you wanted to calculate this ϕ_i information, okay? So, this equation is going to be very much essential and then you are expected to remember this equation during the entire course of this advanced thermodynamics course for the entire semester.

Now, this equation enables to estimate fugacity coefficient at constant temperature and composition via volumetric data or we can calculate the effect of pressure on the fugacity

coefficient or fugacity of a given component i in the mixture provided if you know the volumetric data in the volume explicit form that is V = F_v (temperature, pressure, and composition), it has to be explicitly in this form, right? You have an equation of state something like Redlich-Kwong equation, but you cannot write that Redlich-Kwong equation as volume explicit form.

Volume explicit form in the sense left hand side you should have only volume terms and on the right hand side all other terms other than volume terms should be there. So, Redlich-Kwong equation you cannot write in such kind of format. So, then how to do that one? For that case, we will be taking you know fugacity coefficient estimation by taking temperature and volume as independent variables, those things anyway we are going to do later on.

So, now for the time being, this equation is very much essential and then it is used to find out the fugacity coefficient of component i in the mixture provided you know the volumetric data in the form of volume explicit form as function of temperature, pressure, and composition, okay?

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Now if you have a pure component. If you have a pure component, then partial molar volume is nothing but molar volume if it is simply one single component is there as a pure state, right? Then whatever the equation 14 that we have developed, you know, equation 14 is nothing but this $RT \ln \dfrac{fi}{yi\, P} = \int_0^P \left(\bar{v}i - \dfrac{RT}{P} \right) dP$, whatever the equation just we derived equation number 14. So, this equation in place of the $\bar{v}_i$ we have to write v_i and then it is pure component, so $y_i = 1$.

So, that is $RT \ln \frac{fi}{P}$ and then it is pure i, so just to differentiate f_i from the f_i of a component in the mixture what we are writing, we are using subscript pure i like this, okay?

So, $RT \ln\left(\frac{fi}{P}\right)_{\text{pure i}} = \int_0^P \left(\bar{v}i - \frac{RT}{P}\right) dP$, okay? Where v_i is nothing but the molar volume of pure i. So, this is the equation that $\ln\left(\frac{fi}{P}\right)_{\text{pure i}} = \int_0^P \frac{1}{RT}\left(\bar{v}i - \frac{RT}{P}\right) dP$ if you wanted to know the fugacity coefficient or fugacity of pure component i which is non-ideal, okay?

So, this equation we have to use. Remember this equation number 14 that is for a component i in a mixture is useful when the mixture is non-ideal, okay? Obviously if it is ideal, then $\phi_i=1$. Similarly, if it is not a mixture but a pure component i, then if you wanted to know its fugacity, then you can use this equation number 16 provided that that particular pure gas is in a kind of a non-ideal behavior that is having some amount of non-ideality, okay?

The same equation we can write in terms of the compressibility because we know $\frac{vi}{RT} - \frac{1}{P}$ this particular thing and then if I multiply by P and divide by P this equation, then I can have on the right hand side $\int_0^P \left(\frac{P\bar{v}i}{RT} - 1\right)\frac{1}{P} dP$ and then we know this $\frac{PV}{RT}$ = compressibility factor Z, so we can have $\ln\left(\frac{fi}{P}\right)_{\text{pure i}} = \int_0^P \frac{Z-1}{P} dP$, this we can make use, okay? So, both equation number 16 and this equation are same but only thing that this equation is written in terms of compressibility, right?

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So, we have seen if we know that V as function of temperature, pressure, and composition and then taking temperature and pressure as independent variable, so we can find out the fugacity coefficient but what is this function, we have to know. If it is ideal behavior, then we know this V as $V = \frac{RT}{P}$ because PV = RT for the ideal behavior. If it is non-ideal behavior, then what is that relation? What are the extra terms coming into the picture because of the non-ideal behavior, all those things one should know, and then how we can know those things? We can know only based on the molecular concentration.

There is no thermodynamics involved in order to get this information. We can know this information only by experiments or by the molecular consideration, okay? So, one can easily calculate fugacity of any substance in a mixture using equation 14 provided the function of F that is given any equation 15 is known, right? But this is the main difficulty, what is F? And F need not be an analytical function. In general, sometimes tabulated volumetric data are available for individual pure gases that may be differentiated and integrated numerically to yield the desired thermodynamic functions F that is one possibility.

But this is rarely the case especially for mixtures because this volumetric data informations are available for mostly for kind of pure gases, not for the mixtures. Then usually one must estimate volumetric behavior from limited experimental data that is available. Generally no valid equation of state applicable to large number of pure substances and their mixtures over a large number of conditions including the liquid phases, so that means we have a large number of models.

So, we have to take one by one and then use that equation number 14 by writing those you know equations of state in a volume explicit form and then by using that volume explicit form of the equation of state, find out $\overline{v}_i$, substitute $\overline{v}_i$ in equation number 14 and get information about the fugacity coefficient of any component i, okay? But as you know the data is so vast and diversified the data as you know variations are so many that it is not possible to have a kind of one single model which is suitable for large number of pure substances and their mixtures over a large number of conditions that is not possible.

There are some good equations of state useful for only limited class of substances and then for limited conditions. However, these equations are almost always pressure explicit form rather

than the volume explicit form as I was mentioning that Redlich-Kwong equation. This equation if you see you can write it as a kind of a pressure explicit form but you cannot write as a kind of volume explicit form. So, because of this reason for Redlich-Kwong equation, we cannot use the equation number 14, this is for an example.

There may be other cases, many cases also. So, then what we have to do? We have to develop similar kind of relations for a fugacity coefficient as temperature and volume as independent variable, right? Then under such conditions let us say you can write those equations of state in a pressure explicit form and then whatever that equation that we get for the fugacity coefficient as temperature and volume as independent variables in that equation, we can do the simplification and get this one.

Anyway, this one we are going to do in the next lecture. If you have this equation of state in pressure explicit form, then what fugacity coefficient ϕ_i is? This we are going to do in the next lecture.

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Fugacity of a component in a mixture of ideal gases that we already know for i^{th} component of an ideal gas mixture, the fugacity is nothing but its partial pressure, okay? But however, we can prove from this equation again. So, if we have an ideal gas mixture, then $Pv = RT$. So, this we can write $\frac{PV}{nT} = RT$, v as I mentioned already that is molar basis, v is the volume, V is the total volume. So, this $V = \frac{nT\,RT}{P}$, I can write like this in this form as a given in equation number 19.

Now what we want, we want $\bar{v}_i$ that is $\left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_j}$. So, this equation if you do partially differentiation with respect to n_i, you can get it is nothing but $\frac{RT}{P}$. Let us say i = 1, then $\frac{RT}{P}$ $\left(\frac{\partial n_1}{\partial n_1} = 1\right) + \frac{\partial n_2}{\partial n_1}$ and all those things are you know will be 0. So, that is the reason the $\bar{v}_i$ for this case is nothing but $\frac{RT}{P}$. So, this is the equation number 14. You know in the equation number 14, what we have RT ln $\frac{f_i}{y_i P}$ $= \int_0^P (\bar{v}_i - \frac{RT}{P})$ dP we are having.

So in place of $\bar{v}_i$, we can write $\frac{RT}{P}$ and that means you know $\frac{RT}{P}$ - $\frac{RT}{P}$ = 0. So, what we get $\frac{f_i}{y_i P}$ = 1 that means $f_i = y_i$ P, right? So, this is the limiting condition or limiting basis that we have taken in defining this auxiliary functions activity coefficient and fugacity coefficient though we know we have to get back because these are the basis that we have taken to define these auxiliary functions. That is for a mixture of ideal gases, the fugacity of i is equals to its partial pressure.

Now, we take a mixture of real gases, right? And then try to obtain what is the fugacity coefficient but the mixture of real gases we are taking such a way that they are isothermally mixed such a way that there is no change in volume that is V Σ n_i v_i, okay? So, this is known as the kind of Amagat's law. If there is no change in volume when the different gases are mixed isothermally and then obeying that there is a linear relation between V and then v_i, then we call it as a kind of Amagat's law.

Then from there whatever the fugacity coefficient, etc., we get some kind of new expression we call it as a kind of a Lewis fugacity rule that we are deriving now.

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Lewis fugacity rule

- Assume that the gas mixture follows Amagats's law at all pressures (i.e., real gases) up to the pressure of interest.
- Amagat's law states that at fixed T & P, the volume of mixture is a linear function of mole numbers $\Rightarrow V = \sum_i n_i v_i$ \hfill (22)
- Here also v_i is molar volume of pure i at same T & P and in same phase
- Another way to state Amagat's law is to say that at constant T & P, the components mix isothermally, i.e., with no change in the total volume
- If there is no volume change, then partial molar volume of each component must be equal to its molar volume in the pure state

$$V = \sum n_i v_i$$

$$\bar{v}_i = v_i \quad \Leftarrow \quad \frac{\partial V}{\partial n_i} = \bar{v}_i = \frac{\partial}{\partial n_i} \sum n_i v_i = v_i$$

Assume the gas mixture follows Amagat's law at all pressure that is real gases. If it is ideal gas, then it is valid only at low pressures P tends to 0 and then up to the pressure of interest, okay? Amagat's law states that at fixed temperature and pressure, the volume of mixture is a linear function of mole numbers that is V = Σ n_i v_i, okay? That means, in this case here v_i is nothing but molar volume of pure i at same temperature and pressure and in the same phase whichever phase we are taking.

Another way to state Amagat's law is to say that at constant temperature and pressure, the components mix isothermally that is with no change in the total volume. If there is no change in the total volume, then obviously what we can say? We can say that partial molar volume is nothing but the molar volume of that particular component that is V = Σ n_i v_i. So, $\frac{\partial V}{\partial ni} = \bar{v}_i$.

So, from here what we do? If you do $\frac{\partial}{\partial ni}$ Σ n_i v_i, then you will get v_i that means what we get from here $\bar{v}_i$ is nothing but v_i that is partial molar volume is nothing but the molar volume of that particular component, okay?

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- By differentiating equation (22) ➔ $\bar{v}_i = \left(\dfrac{\partial V}{\partial n_i}\right)_{T,P,n_j} = v_i$ (23)

- Substitute above equation in equation (14) gives:

$$RT \ln\left(\frac{f_i}{y_i P}\right) = \int_0^P \left(v_i - \frac{RT}{P}\right) dP \qquad (24)$$

- Compare above equation with equation (16) for pure substance, i.e.,

$$RT \ln\left(\frac{f_i}{P}\right)_{pure\ i} = \int_0^P \left(v_i - \frac{RT}{P}\right) dP \qquad (16)$$

$$\Rightarrow f_i = y_i\, f_{pure\ i} \qquad (25)$$

- This equation is known as Lewis fugacity rule

So, this we make use in the equation number 14, right? So, equation number 14 is what RT ln $\frac{fi}{yi\ P} = \int_0^P (\bar{v}i - \frac{RT}{P})$ dP. So, in place of $\bar{v}_i$, now we can write v_i because V = Σ n_i v_i. Now, compare above equation with the equation 16 for pure substances. What is that we are having in equation 16 that is pure substance that is RT ln ($\frac{fi}{P}$) pure i $= \int_0^P (vi - \frac{RT}{P})$ dP that is what we just derived. So, this is what we have the equation number 16, okay?

Now, if you compare equation number 24 that is for a real gas mixture, you know obeying Amagat's law and then this equation number 16 that is for a pure substance. So, then what we can understand by comparing these 2 equations, right hand side of these 2 equations are same. So, then if you compare this equation and then similarly equate the left hand side of this equation, then we get $\frac{fi}{yi\ P} = (\frac{fi}{P})$ pure i that is what we get. That means, f_i = y_i $f_{pure\ i}$. This is known as the Lewis fugacity rule.

That means, if the real gases are mixed isothermally and there is no change in volume by mixing that is V = Σ n_i v_i that Amagat's law is being applicable, then under such conditions if you know the fugacity of pure component i, then you do not need to do original calculation to find out its fugacity it in a mixture of gases. Simply what you have to do? You have to multiply the known fugacity of pure component i with the volume fraction of that particular component in the mixture, so that you get fugacity coefficient of that particular component i in a mixture, okay?

So, that is $f_i = y_i f_{pure\ i}$, f pure i is nothing but fugacity of pure component i and then f_i is nothing but fugacity of component i in a mixture of gases, okay?

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Now, what we take fugacity of a component in a mixture at moderate pressure that is the important of the equation number 14. $RT \ln \phi_i = \int_0^P (\bar{v}i - \frac{RT}{P})\ dP$ that relation that we derived. Importance of that relation is that that we can make use of that equation for the cases where there is a non-ideality. Non-ideality is there, you know beyond the low pressure condition that is moderate to high pressure conditions. So, we take a case of moderate pressure condition and then we take certain equation of state and then we apply this equation number 14 to find out fugacity coefficient, okay? That is what we are going to do.

Let us compute the fugacity of a component in a binary mixture at moderate pressures. Consider a form of Van der Waals equation valid only to moderate pressures. So, Van der Waals equation what we have? We have Van der Waals equation $PV = RT + \left(b - \frac{a}{RT}\right) P + ...$ P square, P cube terms will also be there, but we are taking moderate pressure and then we are interested to consider only this part, let us not worry about the P square, P cube terms.

Now, if it is a kind of ideal behavior, then PV should be RT, there should not be any additional terms. There is a non-ideality because of the moderate pressure. So, because of that non-ideality, there is a kind of additional term here that is that additional term is nothing but $\left(b - \frac{a}{RT}\right)$. There are more additional terms as you know in terms of P square, P cube. But

we are not taking them. So, because of this non-ideality in the system brought in terms of these additional term, how the fugacity coefficient is going to change?

Fugacity coefficient has to be 1 for ideal gases or ideal gas mixtures. But it is not for the non-ideal cases. Now, we brought in non-ideality in the gas system by using this Van der Waals equation of state, okay? Now, here this a and b are nothing but Van der Waals constants, right? And these a and b constants that is Van der Waals constants are available only for pure system, only for pure gases they are available, right? Let us take nitrogen gas at moderate pressure and there exist a non-ideality.

For the sake of simplicity, let us take that case and then that non-ideality or whatever the volumetric data of that nitrogen with respect to temperature, pressure and then composition is there with respect to the temperature, pressure, whatever volumetric data is there that if you make a kind of equation form, then this Van der Waals equation of state is you know valid. Then under such conditions, how to find out this fugacity coefficient that we have to do, right?

So, this a and b are available purely for nitrogen, they may be purely available for oxygen like that, but if you have nitrogen and oxygen, then for the mixture this a an b constants are not available, but these a and b constants for the mixtures are dependent on the composition, how much N_2 you have taken, how much O_2 you have taken that makes a difference in this a, b values. So, that is the reason this a and b values are available for pure components and for you know mixtures, we have to obtain by using some mixing rules.

We have some mixing rules, those things also will see now. So, where and b are Van der Waal's constant for the mixture, okay? So, now this equation if you write v which is nothing but V by n_T, molar volume v is nothing but total volume by total number of moles that you apply here and then you write this equation in volume explicit form because we want this equation in a volume explicit form, so that from here we can find out $\bar{v}_i = \frac{\partial V}{\partial n_i}$ and then substitute in equation number 14 and get the required fugacity coefficient relations for this equation of state, okay?

Let us have subscript 1 and 2 for 2 components. For simplicity, we are starting with a binary mixture at moderate pressure, okay? Then $\bar{v}_1$, so we find out what is ϕ_1. So, we have to know what is $\bar{v}_1$, $\bar{v}_1$ is nothing but $\frac{\partial V}{\partial n_1}$ at constant temperature, pressure, and n_2, there are only 2

components, so n_1 and n_2 are the only moles are present, okay? This is nothing but you know partially differentiate this equation $V = \dfrac{nTRT}{P} + n_Tb - \dfrac{nTa}{RT}$, then you will get $\bar{v}_1$.

So that is $\dfrac{\partial}{\partial n1}\left(\dfrac{nTRT}{P}\right) = \dfrac{RT}{P} + \dfrac{\partial}{\partial n1}(n_Tb)$ that we do not know because what is this b for mixture we do not know as of now. Then last term is $\dfrac{1}{RT}\dfrac{\partial}{\partial n1}(n_Ta)$, so simply this is what we are getting $\bar{v}_1$, okay? So, as I mentioned this a and b are you know dependent on the composition for mixtures. So, there are many mixing dose are there.

For simplicity now, for the time being we are taking this constant a for the mixture, right? a is a function of composition and constants of a pure species, a_1 is nothing but the constant a of gas 1 and then a_2 is nothing but constant a for gas 2 and then a is nothing but the constant a for the mixture of gas 1 and gas 2, right? So, these are dependent on the composition of the mixture, so this $a = y^2{}_1a_1 + 2\, y_1\, y_2\, \sqrt{(a1a2)} + y^2{}_2a_2$, this is what we get, okay? So now, similarly b of the mixture is related to the b of gas 1 that is b_1 and b of gas 2 that is b_2.

How it is related? It is related to the composition and then it is given as b of mixture = $y_1\, b_1 + y_2\, b_2$, y_1 and y_2 are nothing but the mole fraction of component 1 and 2 that are present in the mixture, okay?

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So, $y_1 = \dfrac{n1}{nT}$ and $y_2 = \dfrac{n2}{nT}$. So, from here that mixing rules, whatever $a = a_1\, y^2{}_1 + 2\, y_1\, y_2\, \sqrt{(a1a2)} + a_2\, y^2{}_2$ in this relations, we are writing $y_1 = \dfrac{n1}{nT}$ and $y_2 = \dfrac{n2}{nT}$, then we get this equation that is

$a = \frac{(n1^2 a1 + 2\, n1\, n2\sqrt{(a1 a2)} + n2^2 a2)}{nT^2}$. So, one of the n_T I have taken to the left hand side because we wanted to find out $\frac{\partial}{\partial n1}(n_T a)$ so that to find out $\bar{v}_1$.

Then, similarly $b = \frac{n1}{nT\, b1} + \frac{n2}{nT\, b2}$. So one of the n_T that we are taking to the left hand side and $n_T b = n_1 b_1 + n_2 b_2$ so that we can get $\frac{\partial}{\partial n1}(n_T b)$ which is required to get v_1. So, when we partially differentiate this $n_T a$ and $n_T b$ with respect to n_1 and then simplify, we get this expression, right?

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Similarly, the b, whatever the b relation that we have $b = \frac{n1\, b1}{nT} + \frac{n2\, b2}{nT}$, this we partially differentiate with respect to n_1 by keeping temperature, pressure and two constant then we get $b_1 + 0 = b_1$. Now, these 2 quantities, we substitute this equation number 28 that is nothing but $\bar{v}_1 = \frac{RT}{P} + \frac{\partial}{\partial n1}(n_T b) - \frac{1}{RT}\frac{\partial}{\partial n1}(n_T a)$. Now, these 2 we just evaluated by using the mixing rules. So, we substitute here, then we have this relation, right?

So, now this relation, what we do? We substitute in equation number 14 that is $\ln \phi_i = \frac{1}{RT}\int_0^P (\bar{v}1 - \frac{RT}{P})\, dP$, we are doing for component 1. So, here in place of $\bar{v}_1$, whatever you are getting from this equation number 33, you substitute here, then we will have this expression when you substitute $\bar{v}_1$. So, this is all nothing but $\bar{v}_1$. Now, here this $\frac{RT}{P}$ and then this $-\frac{RT}{P}$ may be cancelled out. So, under the integration only this part is remaining.

Then, we have $\ln \phi_1 = \ln \frac{f_1}{y_1 P} = \frac{1}{RT} \int_0^P \frac{RT}{P} + b_1 - \ldots$, this particular term, dP, right? Now, this b_1, b_2, a_1, a_2 are independent of the pressure, okay? So, then what we can do? When we integrate, we can get you know integral of dP sP because all this entire thing is constant for a given constant temperature and composition, right? So, then we can get b_1 P - this particular term multiplied with P.

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$$\Rightarrow \ln \phi_1 = \frac{1}{RT}\left\{ b_1 P - \frac{1}{RT}\left[\frac{n_T(2n_1 a_1 + 2n_2\sqrt{a_1 a_2}) - a n_T^2}{n_T^2} \right] \cdot P \right\}$$

$$\ln \phi_1 = \frac{1}{RT}\left\{ b_1 P - \frac{P}{RT}\left[\frac{2n_1 a_1}{n_T} + \frac{2n_2\sqrt{a_1 a_2}}{n_T} - a \right] \right\}$$

$$= \frac{1}{RT}\left\{ b_1 P - \frac{P}{RT}[2a_1 y_1 + 2\sqrt{a_1 a_2} \cdot y_2 - a_1 y_1^2 - 2y_1 y_2 \sqrt{a_1 a_2} - y_2^2 a_2] \right\} \checkmark$$

$$= \frac{1}{RT}\left\{ b_1 P - \frac{P}{RT}[a_1(2y_1 - y_1^2) + 2\sqrt{a_1 a_2} \cdot (y_2 - y_1 y_2) - a_2 y_2^2] \right\}$$

$$= \frac{1}{RT}\left\{ b_1 P - \frac{P}{RT}[a_1 y_1(2 - y_1) + 2\sqrt{a_1 a_2} \cdot y_2(1 - y_1) - a_2 y_2^2] \right\}$$

$$= \frac{1}{RT}\left\{ b_1 P - \frac{P}{RT}[a_1 y_1(1 + y_2) + 2\sqrt{a_1 a_2} \cdot y_2^2 - a_2 y_2^2] \right\}$$

So, that is what this term, by integrating and substituting 0 to the limits. So, this term and this term both of them are independent of P. So, integral of dP sP and then limits 0 to P. So, P - 0 is P, so that P we are substituting here, right? So, now, this equation further we can write it like this by taking this n_T and n_T^2 you can cancel, so that we can write like this. Why are we doing this one? Because we have this $\frac{n_1}{n_T}$ terms into $\frac{1}{n_T}$ terms, so for those terms we can write y_1 y_2. So, let us write y_1 y_2 for those terms.

So, that is $2 a_1 y_1 + 2\sqrt{(a_1 a_2)}$ and then y_2 and then - a we can write - $a_1 y_1^2 + 2 y_1 y_2 \sqrt{(a_1 a_2)} + a_2 y_2^2$. So, this is nothing but a by mixing rules, right? So, why are we doing? Because I wanted to write this equation only in terms of temperature, pressure, and then constant a_1, a_2, b_1, b_2 and composition y_1 y_2, okay? Now further what we do? We simplify this equation such a way that we have only y_2 terms.

So, that you know it will be easy to check whether you know under limiting conditions y_2 tends to 0 what is the fugacity coefficient for pure component as well that is the purpose, okay? Or otherwise this part is final, okay? Further simplification may not be required, okay? So that to

have a kind of limiting conditions from the point of view of pure substance, we simplify this equation either in the form of function of y_2 or function of y_1, okay? Let us do as a function of y_2.

So, at first what I am doing, a_1 I am taking common from this term and this term, so that a_1 into $2 y_1 - y^2_1$ I can write, and then from these 2 terms, what I am doing I am taking $2\sqrt{(a1a2)}$ as common so that I can have $y_2 - y_1 y_2$ and then remaining this $a_2 y^2_2$ term is as it is. In the next step here, I am taking y_1 common, so that $2 - y_1$ here. From these 2 terms, y_2 I am taking common so that I can have $1 - y_1$ here and then y_2 square as it is. Next step, $2 - y_1$ is nothing but $1 + y_2$ because y_1 is nothing but $1 - y_2$.

In place of y_1, if I substitute $1 - y_2$, I can write $2 - y_1$ as nothing but $1 + y_2$ and then here in the second place, $1 - y_1$ I can write y_2. So, y_2 into y_2, y^2_2 and this term is as it is.

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$$\bullet \ \ln\phi_1 = \ln\frac{f_1}{y_1 P} = \frac{1}{RT}\left\{b_1 P - \frac{P}{RT}[a_1(1-y_2)(1+y_2) + 2\sqrt{a_1 a_2}\cdot y_2^2 - a_2 y_2^2]\right\}$$
$$= \frac{1}{RT}\left\{b_1 P - \frac{P}{RT}[a_1(1-y_2^2) + 2\sqrt{a_1 a_2}\cdot y_2^2 - a_2 y_2^2]\right\}$$
$$= \frac{1}{RT}\left\{b_1 P - \frac{P}{RT}[a_1 - a_1 y_2^2 + 2\sqrt{a_1 a_2}\cdot y_2^2 - a_2 y_2^2]\right\}$$
$$= \frac{1}{RT}\left\{P b_1 - \frac{a_1 P}{RT} + \frac{P}{RT}[a_1 y_2^2 - 2\sqrt{a_1 a_2}\cdot y_2^2 + a_2 y_2^2]\right\}$$
$$= \left(b_1 - \frac{a_1}{RT}\right)\frac{P}{RT} + (\sqrt{a_1} - \sqrt{a_2})^2\cdot y_2^2\frac{P}{(RT)^2}$$
$$\therefore \ \phi_1 = \frac{f_1}{y_1 P} = \exp\left\{\left(b_1 - \frac{a_1}{RT}\right)\frac{P}{RT}\right\}\left\{\exp(\sqrt{a_1} - \sqrt{a_2})^2\cdot\frac{y_2^2 P}{(RT)^2}\right\} \rightarrow (34)$$

- This eq. (34) is for fugacity of a component "i" in a mixture of gases at moderate pressures obeying van der Waals equation of state and it is function of $\phi = \phi(a_1, a_2, b_1, b_2, P, T, y_1, y_2)$

Next step what I can do? This y_1 I can write it as $1 - y_2$, so that $1 - y_2$ into $1 + y_2$. I can write $1 - y^2_2$. So, that is what I have. So, here $1 - y^2_2$ and then remaining 2 terms are as it is, right? So, now, further I can write this one as a_1 and then this remaining terms like this expand $a_1 - a_1 y^2_2$ and then remaining 2 terms are as it is, right? So, now, what I do in next step, this a_1 I take out of the parenthesis so that I can write $b_1 P - a_1 \frac{P}{RT}$ as one term and then remaining terms I can take - common.

So $+ \frac{P}{RT} * a_1 y^2_2 - 2\sqrt{(a1a2)}y^2_2 + a_2 y^2_2$, so that this term I can write as $(\sqrt{a1} - \sqrt{a2})^2$ and then remaining terms are as it is that is $y^2_2 \frac{P}{(RT)^2}$, okay? So, finally

$\ln \phi_1 = b_1 - \frac{a1}{RT} * \frac{P}{RT} + (\sqrt{a1} - \sqrt{a2})^2 y^2_2 \frac{P}{(RT)^2}$

Or, $\phi_1 = f_1 y_1 P = \exp\left\{\left(b1 - \frac{a1}{RT}\right)\frac{P}{RT}\right\}\left\{\exp(\sqrt{a1} - \sqrt{a2})^2 . \frac{y2^2 P}{(RT)^2}\right\}$.

So, now we can see if it is the ideal gas behavior, then ϕ_1 should be equals to 1, but now it is not ideal because of the moderate pressure there is non-ideality. Because of non-ideality, there are 2 corrections in the form of exponential terms like this and what we can see? The first exponential term is independent of composition is also independent of $a_2 b_2$ constants of pure gas 2, remember $a_1 b_1$ for constants of pure gas 1 and $a_2 b_2$ are nothing but the constant for pure gas 2, where a and b are for mixtures and this we obtained by the mixing rule.

Now we can see this first correction is independent of second component, it is constant, its mole fraction nothing is coming into the picture, whereas the second term is function of you know both first component in terms of a_1, a_2 as well as y_2 as well, okay? So, if the non-ideality of a gaseous mixture is represented by the Van der Waals equation in the volume explicit form and then if you take the volume explicit form, only first pressure term P square, P cube terms are neglected.

Then fugacity of component 1 if it is a binary mixture, then we can get this one as a kind of fugacity of that particular component in the binary mixture, right? So, we can see this ϕ is function of a_1, a_2, b_1, b_2, P, T, y_1, y_2 which are excellent experimentally measurable quantities. Temperature and pressure you can measure, composition you can measure, a_1, a_2 b_1, b_2 also you can measure. So, auxiliary function fugacity is directly related to the temperature, pressure, and then composition of the system without any difficulty, whereas chemical potential we are unable to develop such kind of relations.

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$$\phi_1 = \frac{f_1}{y_1 P} = \exp\left[\left(b_1 - \frac{a_1}{RT}\right)\frac{P}{RT}\right]\exp\left[\frac{\left(a_1^{1/2} - a_2^{1/2}\right)^2 y_2^2 P}{(RT)^2}\right]$$

- **Correction for non-ideality: first exponent independent of component 2 but not the second exponent as it contains a_2 & y_2.**
- **As $y_2 \to 0 \Rightarrow f_1 \to f_{pure\ 1} = P \exp\left[\left(b_1 - \frac{a_1}{RT}\right)\frac{P}{RT}\right]$ (35)**
- **Substitute above equation (35) in equation (34)**

$$\Rightarrow f_1 = y_1 f_{pure\ 1} \exp\left[\frac{\left(a_1^{1/2} - a_2^{1/2}\right)^2 y_2^2 P}{(RT)^2}\right] \quad (36)$$

- **This exponent term is correction for Lewis fugacity rule given by equation (25)** $f_i = y_i f_{pure\ i}$

Now, correction for non-ideality. First exponent independent of component 2, but not the second exponent as it contains both a_2 and y_2. Let us say if you have a pure component 1 that means y_2 tends to 0. If y_2 tends to 0, then the second exponent, whatever the exponent $\left\{(\sqrt{a1} - \sqrt{a2})^2 . \frac{y2^2 P}{(RT)^2}\right\}$, if this $y_2 = 0$, so exponential of 0 that is 1, so the second exponent is 1, on the second term that second correction is 1, okay?

So that means f pure 1 is nothing but P multiplied by $\exp\left\{\left(b1 - \frac{a1}{RT}\right)\frac{P}{RT}\right\}$, right? So substitute above equation in 35, the 35 equation is nothing but whatever that equation that we have derived, so this is the equation number 35, in the previous slide that we derived. So here, we can write $\frac{f1}{y1} = P * \exp\left\{\left(b1 - \frac{a1}{RT}\right)\frac{P}{RT}\right\}$. So, $P * \exp\left\{\left(b1 - \frac{a1}{RT}\right)\frac{P}{RT}\right\} = f_{pure\ 1}$. So, $\frac{f1}{y1} = f_{pure\ 1}$ and then second exponent as it is.

So, $f_1 = y_1\ f_{pure\ 1}\left\{exp(\sqrt{a1} - \sqrt{a2})^2 . \frac{y2^2 P}{(RT)^2}\right\}$, and this expression we know that a $f_i = y_i f_{pure\ i}$ we just derived a few slides before, it is known as the Lewis fugacity rule. Lewis fugacity rule that is obeying you know Amagat's law that is $V = \Sigma\ n_i\ v_i$. Then whatever the f_i is there that is nothing but $y_i * f_{pure\ i}$. Now, here you know in addition to that one, there is a kind of correction because of non-ideality.

Because of non-ideality, there is a correction okay? This exponent term is correction for the Lewis fugacity rule that is given by equation number 25 that is fi = y_i f $_{pure\ i}$, okay? This is how we have to find out the fugacity or fugacity coefficient of any substance in a mixture or a

fugacity coefficient of a pure component by using equation of state. If the equation of state is available, the volumetric data is available in the volume explicit form then equation number 14 we can make use.

Then further the equation of state for that volumetric data whatever volume explicit form is given, you can find out $\bar{v}_i$. That $\bar{v}_i$ you can substitute in equation number 14 to get the fugacity coefficient of that particular component in the mixture, okay? So, similarly we can do some kind of analysis for kind of pressure explicit format also. Those things we see in the next class, but however, what before going to the pressure explicit form. We have to make use of this equation for a pure solid or liquid phase, pure condensed phase.

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Fugacity of a pure liquid or solid:

- We have already seen that equation (16): $\ln\left(\frac{f_i}{P}\right)_{pure\ i} = \int_0^P \frac{1}{RT}\left(v_i - \frac{RT}{P}\right)dP$
- This equation is general and not limited to the vapor phase only.
- It may be used to calculate the fugacity of a pure liquid or that of a pure solid.
- For a pure condensed component at T and P, equation (16) is rewritten as follows:
- $RT\ln\left(\frac{f_i^c}{P}\right) = \int_0^{P_i^s}\left(v_i - \frac{RT}{P}\right)dP + \int_{P_i^s}^P\left(v_i^c - \frac{RT}{P}\right)dP$ (37)
- Where superscript "c" refers to condensed phase and superscript "s" refers to saturated phase
- First term on the right hand side: fugacity of saturated vapor at T and P^s (saturation pressure)
- Second term on RHS: correction due to the compression of condensed phase to pressure P.
- At saturation pressure (P^s), the fugacity of saturated vapor is equal the fugacity of the saturated liquid (or solid) because the saturated phases are in equilibrium.

Now fugacity of a pure liquid or solid. How to find out the fugacity of pure liquid or solid or a condensed phase that is what we are going to see now. We have already seen that $\ln\left(\frac{f_i}{P}\right)_{pure\ i}$ is $\int_0^P \frac{1}{RT}\left(v_i - \frac{RT}{P}\right)dP$ for pure component. If it is a component in a mixture, then $\bar{v}_i$ should be there, since it is a pure component then v_i is here, okay? Now, this equation is general and not limited to the vapor phase only because while deriving this equation, we have not made any assumption on the phase whether it is gas phase, liquid phase, or solid phase.

So, whatever this equation 14 and then 16 that we have derived for the component i in the mixture or pure component i. They are valid irrespective of the phase whether it is a liquid phase, solid phase, or vapor phase because we have not made any assumption while deriving those relations. So, it may be used to calculate the fugacity of a pure liquid or that of a pure

solid as well. So, for a pure condensed component at temperature T and pressure P, equation 16 is written as follows.

Actually the pressures 0 to P whatever it is there, we are breaking in 2 limits, 0 to saturation pressure and then saturation pressure to some pressure P, so that you know 0 to saturation pressure we can have a kind of a vapor phase and then saturation pressure to some pressure of our interest beyond the saturation pressure that is valid for the condensed phase and at the saturation pressure, this vapor phase and then condensed phase are at equilibrium, right? That we know.

So, making use of that information, we are writing this equation in 2 parts like this that is RT ln $\frac{f_i^c}{P}$ = integral 0 to P now I am breaking it to 0 to P_i^s and then P_i^s to P. 0 to P_i^s limit, it is in the vapor phase. So, v_i I am writing and then from P_i^s to P, it is in a condensed form, either liquid or solid, right? So for the condensed form what I am writing in place of v_i, I am writing v_i^c, superscript c I am using for the condensed phase and rest everything is same.

Only thing that 0 to P limit I am changing between 0 to P_i^s and then P_i^s to P because at P_i^s the saturation vapor is in equilibrium with the condensed phase, okay? Where superscript c refers to condensed phase and superscript s refers to saturated phase. First term on the right hand side is nothing but fugacity of saturated vapor at temperature T but the pressure P^s that is saturation pressure, okay?

Second term on RHS is a correction by increasing the pressure causing compression of condensed phase to certain pressure P, by increasing the pressure from P_i^s or beyond P_i^s, you have to do the compression by increasing the pressure, you are increasing it to a certain pressure P. So, there should be some kind of correction that correction is given by the second term, okay? At saturation pressure P^s, the fugacity of saturated vapor is equal to the fugacity of the saturated liquid or solid because the saturated phases are at equilibrium at this saturation pressure point.

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$$RT \ln\left(\frac{f_i^c}{P}\right) = \int_0^{P_i^s}\left(v_i - \frac{RT}{P}\right)dP + \int_{P_i^s}^{P}\left(v_i^c - \frac{RT}{P}\right)dP$$

- ∴ Equation (37) becomes: $RT \ln\left(\frac{f_i^c}{P}\right) = RT \ln\frac{f_i^s}{P_i^s} + \int_{P_i^s}^{P} v_i^c\, dP - RT \ln\frac{P}{P_i^s}$ (38)

$$\Rightarrow RT \ln\frac{f_i^c}{P} = RT \ln\left(\frac{f_i^s}{P_i^s} \times \frac{P_i^s}{P}\right) + \int_{P_i^s}^{P} v_i^c\, dP$$

$$\rightarrow \ln\frac{f_i^c}{P} = \ln\left(\frac{f_i^s}{P}\right) + \int_{P_i^s}^{P}\frac{v_i^c}{RT}dP \Rightarrow \frac{f_i^c}{P} = \frac{f_i^s}{P}\exp\left[\int_{P_i^s}^{P}\frac{v_i^c}{RT}dP\right]$$

$$\rightarrow f_i^c = \frac{f_i^s}{P_i^s} \times P_i^s \exp\left[\int_{P_i^s}^{P}\frac{v_i^c}{RT}dP\right]$$

$$\rightarrow f_i^c = P_i^s \phi_i^s \exp\left[\int_{P_i^s}^{P}\frac{v_i^c}{RT}dP\right]$$
(39)

- Where $\phi_i^s = f_i^s / P_i^s$ is fugacity coefficient of saturated vapor

That means the same equation now, what I am going to do? I am integrating this one. So, this here by definition this part is nothing but RT ln (f_i^s / P_i^s), right? This is the superscript s we are using to differentiate as a kind of saturation pressure conditions, okay? So, that is by definition the first term in the RHS is nothing but RT ln (f_i^s / P_i^s) or RT ln (f_i^s / P_i^s), superscript s stands for the saturated phase and then second term, I am just writing you know as 2 parts, integral v_i^c dP - $\frac{RT}{P}$ dP.

So, integral $\frac{RT}{P}$ dP, I can write it as RT ln P and then limits are from P_i^s to P, so I can write the second term as a kind of RT (ln P / P_i^s). So that now what I can do? I can join this RT ln and this RT ln terms in the right hand side together so that I can have RT ln (f_i^s / P_i^s)* (P_i^s / P). So, this P_i^s is cancelled out and then this remaining term we are keeping as it is because what is this v_i^c we do not know, unless we know it we cannot solve this problem, okay?

So, then we have RT, RT also if you take to the right hand side then ln f_i^c by P = ln (f_i^s / P) + integral (v_i^c /RT) dP, so this one if you take off the ln either side, so then we have f_i^c /P = f_i^s/ P exponential of integral (v_i^c /RT) dP integral from P_i^s to P, right? So then f_i^c = (f_i^s / P_i^s)* P_i^s, what I am doing? I am simply in the right hand side multiplying and dividing by P_i^s, so that (f_i^s/P_i^s) I can write it as ϕ_i^s is that is saturation coefficient of ith component, saturation fugacity coefficient of ith component in a pure state and then remaining exponential term is as it is.

So that this f_i^c in which we are interested, we are interested in finding out the fugacity coefficient of a condensed phase that is f_i^c = P_i^s * ϕ_i^s is fugacity coefficient of is saturation

pressure exponential of this particular term as it is, okay? ϕ_i^s is nothing but fugacity coefficient of saturated vapor.

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Now, the equation 30 previously reflects the fugacity of pure condensed component i at temperature T and pressure P is equal to the saturation pressure P_i^s at temperature T to a first approximation, but there is a correction, indeed there are 2 corrections because the pressure is going beyond the P_i^s. So, the first correction is that fugacity coefficient ϕ_i^s that gives the kind of information or the correction for the deviation of the saturated vapor from ideal behavior, right?

Below the P_i^s, the system is in vapor phase and if that vapor face is having some non-ideality, what is the non-ideality that information one can get by this ϕ_i^s information, right? Then second one is exponential correction also known as the Poynting correction takes into the account that the liquid or solid are the condensed phase at pressure P different from P_i^s because these 2 phases the condensed phase and the vapor phase are at equilibrium only at the saturation pressure, right? But the pressure is beyond the saturation pressure.

So there must be some correction and that correction is nothing but the exponential correction that is there in equation number 39, which is also known as the Poynting correction. That is our exponential of integral (v_i^c/RT) dP whatever is there that is known as the Poynting correction but what is v_i^c, it is obviously function of pressure in general but if the range of pressure is far away from the critical conditions, then we can say that the v_i^c is incompressible or the condensed phase is incompressible.

So, that we can say v_i^c is independent of the pressure and then we can write this exponential simply exponential of $v_i^c \frac{\Delta P}{RT}$ and $\Delta P = P - P_i^s$ like this, okay? So, this is known as Poynting correction, okay? This is true only if the operating temperature and pressure are remote from the critical conditions. If their operating temperature and pressure conditions are away from the critical conditions, then we can say that the v_i^c is independent of the pressure or the condensed phase is a kind of incompressible phase, so that we can say v_i^c is independent of pressure.

So, then we can straightforward integrate that equation, then we can have this Poynting correction in this form, but how much is it important that again one has to find out. How much is it important that depends on the $\Delta P = P - P_i^s$, depending on this magnitude, we can say how much it is important. If it is very small, then exponential of some small quantity is usually 1 or close to 1. If it is very large, then it may be contributing something. So, how much small is that we have to make sure.

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Both corrections are often but not always small and sometimes they are negligible as well. If the vapor phase is not very non-ideal or slightly non-ideal, so then ϕ_i may be close to 1, so it may be small, so then you can neglect and then if delta is very small, it is not very large then also exponential correction factor that is Poynting correction is also small. So, in such case also the second correction may also be negligible, right? If temperature T is such a way that the saturation pressure P_i^s is low, say less than 1 bar, then ϕ_i^s is very close to unity.

Because if the saturation pressure is close to 1 bar or less than 1 bar, so then obviously it is possible that vapor phase obeying the ideal behavior and then since ideal behavior is obeyed. Obviously by ϕ_i^s is going to be 1 or close to 1, okay? Now, we see significance of Poynting correction by taking some pure, condensed and incompressible substance of molar volume 100 centimeter cube per mole at 300 Kelvin temperature in order to check how much important is Poynting correction, okay?

Now if the pressure in excess of saturation pressure that is pressure in excess of saturation pressure in the sense $P - P_i^s$ whatever the ΔP is there, that $\Delta P = 1$, then Poynting correction that is exponential of $v_i^c (P - P_i^s)/ RT$, this if you calculate by taking $v_i^c = 100$ cc per mole, then you will get 1.00405 if $\Delta P = 1$. If ΔP is 10, then also it is 1.0405, only approximately 4, so that means we can say still small. So, if Poynting correction is 1 or close to 1, we can say that it is negligible.

But now you can see when ΔP increases to the 100, we can say it is 1.5, Poynting correction is 1.5 and ΔP increases to 1000, then you can say it is 57. So, we can say if the ΔP is small, less than 10 bar or something like that, then we can say that Poynting correction is very small and then if you say the pressure or ΔP is less than 1 bar, so then we can say it is almost negligible.

That means at low pressures, the Poynting correction is small and thus can be negligible but it becomes larger at high pressures and are at low temperatures. So in the next class, we will be discussing a few problems based on the things that we have discussed in this particular lecture. **(Refer Slide Time: 01:17:23)**

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Thank you.