Chemical Engineering Thermodynamics
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Lecture-39
Chemical potential of ideal gas mixtures

Welcome back, in the last lecture our discussion was mainly on the ideal gas mixtures and the properties of ideal gas upon mixing.

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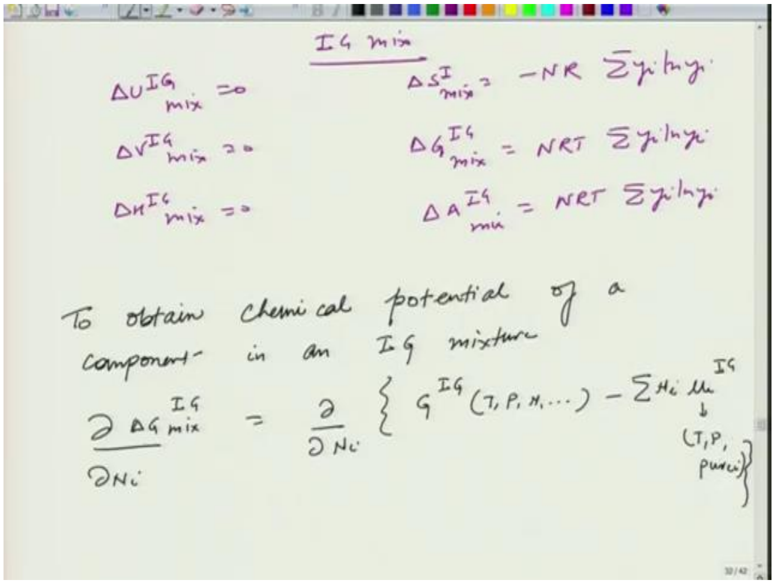

IG mix

$\Delta U^{IG}_{mix} = 0$ $\quad$ $\Delta S^{I}_{mix} = -NR \sum y_i \ln y_i$

$\Delta V^{IG}_{mix} = 0$ $\quad$ $\Delta G^{IG}_{mix} = NRT \sum y_i \ln y_i$

$\Delta H^{IG}_{mix} = 0$ $\quad$ $\Delta A^{IG}_{mix} = NRT \sum y_i \ln y_i$

To obtain chemical potential of a component in an IG mixture

$$\frac{\partial \Delta G^{IG}_{mix}}{\partial N_i} = \frac{\partial}{\partial N_i}\left\{ G^{IG}(T,P,N_1,\dots) - \sum N_i \underset{(T,P,\text{pure})}{\underset{\downarrow}{\mu_i^{IG}}} \right\}$$

And we summaries that for ideal gas mixtures the delta U of ideal gas is going to be 0 upon mixing. Similarly, the delta V has to be 0, delta H has to be 0. However, the entropy is, change in entropy is not 0 and subsequently we have the relation that delta S of ideal gas is nothing but NR summation yi ln yi with a negative sign, okay. Because it has to increase and this is going to be negative and hence, you have positive delta S here. Now considering this to be positive the rest of the things will be also non zero.

$$\Delta U^{IG}_{mix} = 0 \qquad \Delta S^{I}_{mix} = -NR\sum y_i ln\, y_i$$

$$\Delta V^{IG}_{mix} = 0 \qquad \Delta G^{IG}_{mix} = NRT\sum y_i ln\, y_i$$

$$\Delta H^{IG}_{mix} = 0 \qquad \Delta A^{IG}_{mix} NRT = y_i \ln \sum y_i$$

Delta G and delta A are the free energies here. Now I would like to take it forward. Now we would like to get an expression of chemical potential of a component in an ideal gas mixture, okay. So how do you do that, so let us start with basic definition, so I am going to take delta of delta G IG mix, so I am taking a partial derivative of delta G with respect to Ni, okay. And this is nothing but del by del Ni and by definition delta G mix me know is G of IG and since it is a mixture, let us assume that is one than one component, right. Minus summation Ni and this would be your UI. This is ideal gas and this is at temperature T, P and this is for the pure I, right.

So let me use a different symbol here for this, so this is going to be something like this, right. Okay, so what we are doing here is, we are taking the partial derivative of delta G IG mix which is nothing but the gas free energy of the ideal gas mixture, minus that contribution from the pure component that is for NI UI, UI is nothing but a molar free energy of the pure component here, okay, that is what is written here U is the function of T, P and pure I, okay.

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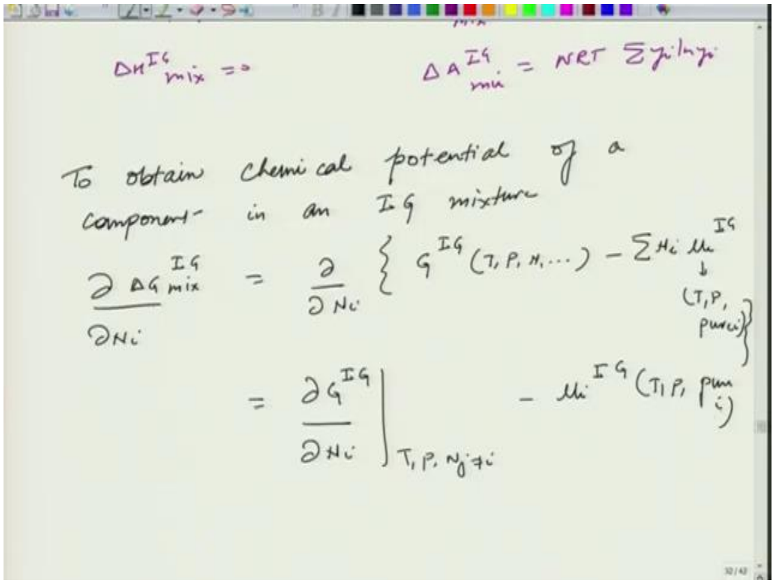

$\Delta H^{IG}_{mix} = 0$ $\Delta A^{IG}_{mix} = NRT \sum y_i \ln y_i$

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$$\frac{\partial \Delta G^{IG}_{mix}}{\partial N_i} = \frac{\partial}{\partial N_i}\left\{ G^{IG}(T,P,N,\dots) - \sum N_i \underset{(T,P,\ \text{pure } i)}{\underset{\downarrow}{\mu_i^{IG}}} \right\}$$

$$= \left.\frac{\partial G^{IG}}{\partial N_i}\right|_{T,P,N_{j\neq i}} - \mu_i^{IG}(T,P,\text{pure } i)$$

So if you tick the derivative here what you are going to get is the following del G IG by del NI temperature T, P, NJ not equal to I, okay. Minus UI of IG at T, P and then it is a pure I, correct.

$$\frac{\partial \Delta G^{IG}_{mix}}{\partial N_i} = \frac{\partial}{\partial N_i}\{G^{IG}(T,P,N,\dots) - \sum H_i \mu_i^{IG}(T,P,pure\ i)\}$$

$$= \frac{\partial G^{IG}}{\partial N_i}\Big|_{T,P,N_{j\neq i}} - \mu_i^{IG}(T, P, pure\ i)$$

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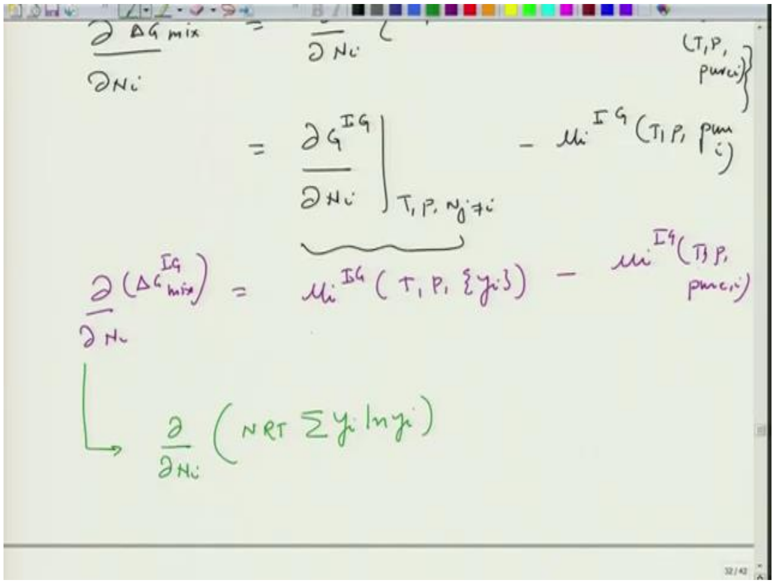

$$\frac{\partial \Delta G_{mix}}{\partial N_i} = \frac{\partial}{\partial N_i}\Big(\qquad (T, P, pure\ i)\Big\}$$

$$= \underbrace{\frac{\partial G^{IG}}{\partial N_i}\Big|_{T,P,N_{j\neq i}}} - \mu_i^{IG}(T, P, pure\ i)$$

$$\frac{\partial(\Delta G^{IG}_{mix})}{\partial N_i} = \mu_i^{IG}(T, P, \{y_i\}) - \mu_i^{IG}(T, P, pure\ i)$$

$$\hookrightarrow \frac{\partial}{\partial N_i}\left(NRT \sum y_i \ln y_i\right)$$

$$\frac{\partial}{\partial N_i}\left(\Delta G^{IG}_{mix}\right) = \mu_i^{IG}(T, P, \{y_i\}) - \mu_i^{IG}(T, P, pure\ i)$$

So now you have this expression and this, this one is going to be nothing but UI because it is a partial, the derivative of the free energy with respect to NI, so this is the UI of I of ideal gas at T, P and the compositions all the mole fraction, so I can also write like YI is minus of course UI, IG, T, P pure, right. So this is your del by del NI, right, delta G IG mix, okay. But you already calculated delta G mix, right, that is this term.

So I am going to now put this on a left hand side and obtain a separate relation here, so I am going to use this as, this is nothing but del by del NI, NRT summation YI, NY, right. So, if you do this, so right-hand side is very clear, it is a change in the chemical potential with respect to the pure component. Change in the chemical potential of a component type with respect to its pure form, right, at the given temperature pressure. That is the right-hand side clearly it tells you.

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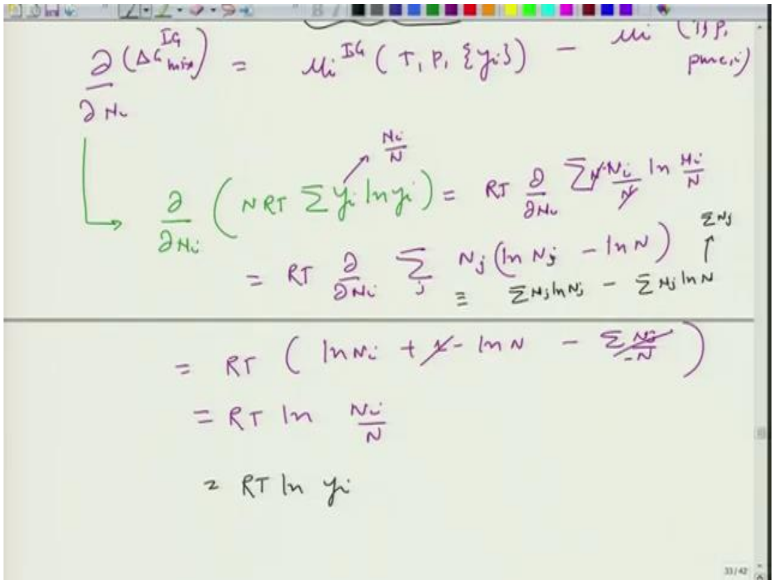

$$\frac{\partial(\Delta G^{IG}_{mix})}{\partial N_i} = \mu_i^{IG}(T,P,\{y_i\}) - \mu_i(T,P,\text{pure } i)$$

$$\frac{\partial}{\partial N_i}\left(NRT\sum \overset{N_i/N}{y_i} \ln y_i\right) = RT\frac{\partial}{\partial N_i}\sum \cancel{N}\frac{N_i}{\cancel{N}}\ln\frac{N_i}{N}$$

$$= RT\frac{\partial}{\partial N_i}\sum_j N_j(\ln N_j - \ln \overset{\sum N_j}{N})$$

$$= \sum N_j\ln N_j - \sum N_j \ln N$$

$$= RT\left(\ln N_i + \cancel{1} - \ln N - \cancel{\frac{\sum N_j}{N}}\right)$$

$$= RT\ln\frac{N_i}{N}$$

$$= RT\ln y_i$$

$$\frac{\partial}{\partial N_i}(NRTy_i ln\, y_i) = \frac{RT\partial}{\partial N_i}\sum N\frac{N_i}{N}ln\frac{N_i}{N} = \frac{RT\partial}{\partial N_i}\sum_j N_j(\ln N_j - \ln N) = RTln\frac{N_i}{N} = RTln\, y_i$$

$$\mu_i^{IG}(T,P,\{y_i\}) - \mu_i^{IG}(T,P,pure\ i) = RTln\, y_i$$

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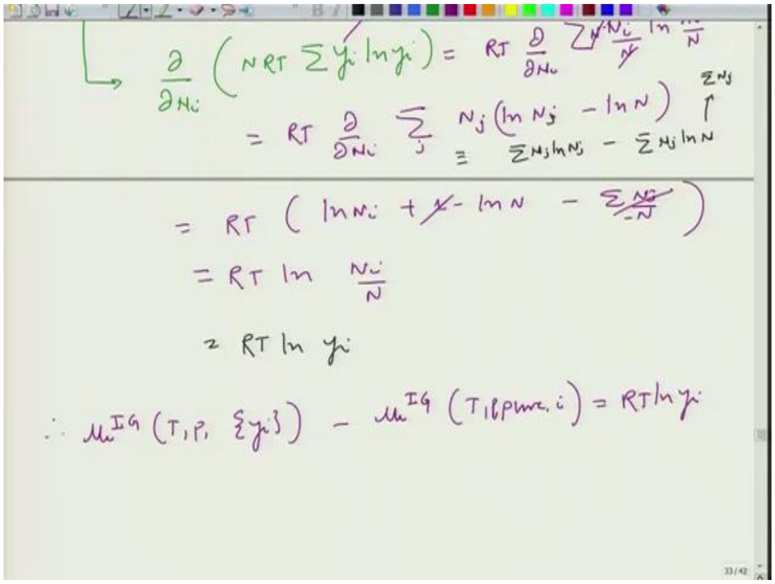

$$\frac{\partial}{\partial N_i}\left(NRT\sum y_i \ln y_i\right) = RT\frac{\partial}{\partial N_i}\sum \cancel{N}\frac{N_i}{\cancel{N}}\ln\frac{N_i}{N}$$

$$= RT\frac{\partial}{\partial N_i}\sum_j N_j(\ln N_j - \ln \overset{\sum N_j}{N})$$

$$= \sum N_j\ln N_j - \sum N_j \ln N$$

$$= RT\left(\ln N_i + \cancel{1} - \ln N - \cancel{\frac{\sum N_j}{N}}\right)$$

$$= RT\ln\frac{N_i}{N}$$

$$= RT\ln y_i$$

$$\therefore \mu_i^{IG}(T,P,\{y_i\}) - \mu_i^{IG}(T,P,\text{pure } i) = RT\ln y_i$$

So that is what you have derived, so therefore, UI IG temperature, pressure YI minus UI IG T pure I that is the temperature pressure and pure I, this would be now RT LN YI, okay. So this your basically the expression which you have developed, okay.

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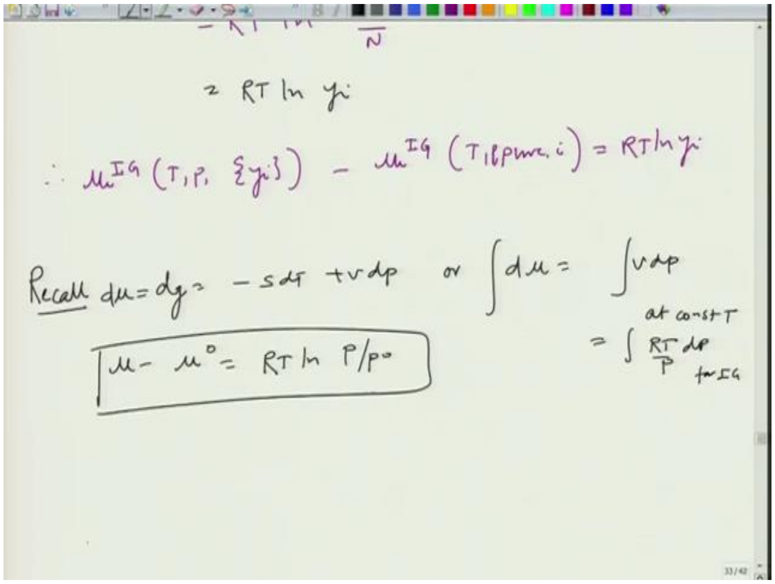

$$= RT \ln y_i$$

$$\therefore \mu_i^{IG}(T, P, \{y_i\}) - \mu_i^{IG}(T, P, \text{pure } i) = RT \ln y_i$$

Recall $d\mu = dg = -s\,dT + v\,dp$ or $\int d\mu = \int v\,dp$ at const T $= \int \frac{RT}{P} dp$ for IG

$$\boxed{\mu - \mu^0 = RT \ln P/P^0}$$

$$d\mu = dg = -sdT + vdP \;\; or \;\; \int d\mu = \int vdP = \int \frac{RT}{P} dP \;\; for\ IG\ at\ const\ T$$

$$\mu - \mu^0 = RT ln \frac{P}{P^0}$$

Now let us look at let or let us recall what we have learned for the case of the pure fluid, okay. And so, if you recall that we have written earlier that DG for the molar case is minus SD plus VDP this is our of course the thermodynamic expression for this and DG is equal to DU this for the case of the pure fluid, right. So I can write that in the following for a constant temperature that DU is integral of VDP at constant temperature or I can write this as DU is equal to VDP at constant temperature and then if I integrate this, okay, then I am going to write like this and this would be your U minus U0.

And for the case for ideal gas I write can this V as RT by P for ideal gas and thus, I can get this expression as RT LN P by P0, right. This we have written earlier also, right. So for the case of a pure fluid and for ideal gas, I can write this expression that the chemical potential difference or chemical potential of the pure component with respect to a reference value is nothing but RT LN P by P0.

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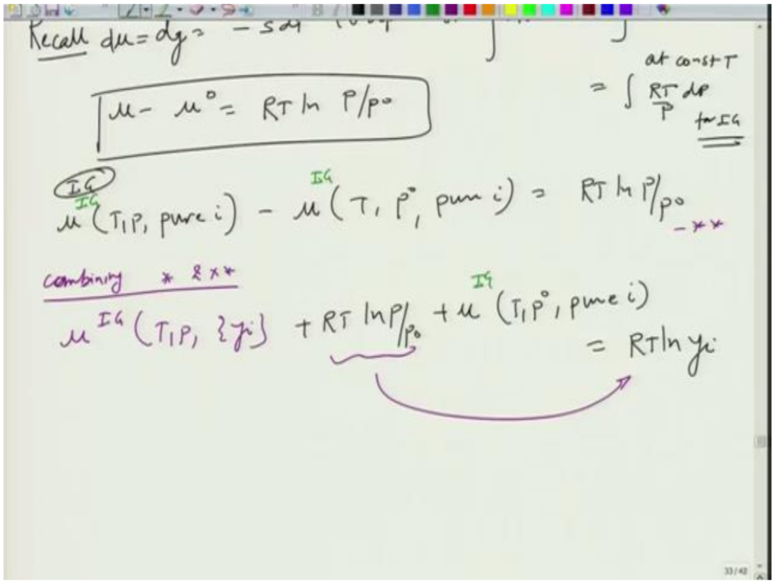

Recall $d\mu = dg = -sdT$

$$= \int \frac{RT}{P} dP \quad \text{at const } T \quad \text{for IG}$$

$$\boxed{\mu - \mu^0 = RT \ln P/P^0}$$

$$\mu^{IG}(T, P, \text{pure } i) - \mu^{IG}(T, P^0, \text{pure } i) = RT \ln P/P^0 \quad -**$$

combining * & **

$$\mu^{IG}(T, P, \{y_i\}) + RT \ln P/P^0 + \mu^{IG}(T, P^0, \text{pure } i) = RT \ln y_i$$

$$\mu^{IG}(T, P, \{y_i\}) + RT ln\frac{P}{P_0} + \mu^{IG}(T, P^0, pure\ i) = RT ln\ y_i$$

$$\mu_i^{IG}(T, P, \{y_i\}) - \mu_i^{IG}(T, P^0, pure\ i) = RT ln\frac{y_i P}{P_0}$$

So here U here is nothing but T, P pure I, right, and U0 is some T some P0 of the same component I, right. So, this is what we have the relation. Now what I am going to do is I am going to use this expression and this expression, these two expressions. And essentially, I will combine it, so instead of just taking a pure I as a reference, I will now take the difference of ideal gas mixtures with respect to a reference state at P0.

So will just like to see what we are going to get there, UI, IG T, P this is something which can remain the same, okay. So, it is like UI T, P summation YI, so we can say here combining star and star, star, okay. So, I am not naming or I am not know numbering the equation here at this point, so I am going to use this only the reference as this. Okay, and then I am replacing this UI IJ by this expression which is RT LNP by P0 plus U0, so because this expression for the ideal gas, so this is also ideal gas, right. So, this for ideal gas, okay.

That is what you are considering here, so I am going to write this as T, P0 pure I, okay, and this has to be equal to RT LN, YI. So you need to rearrange now, okay, so let us look at how to do that, again, I am going to use now make sure that this part is something which can go here, use this as to which was make sure that we are using the same nomenclature. I am going to say that this again ideal gas, this is again ideal gas, so this has to be let us say ideal gas, but it is at the P0 as a reference and this if you put it here minus of this, so this would be, this plus this.

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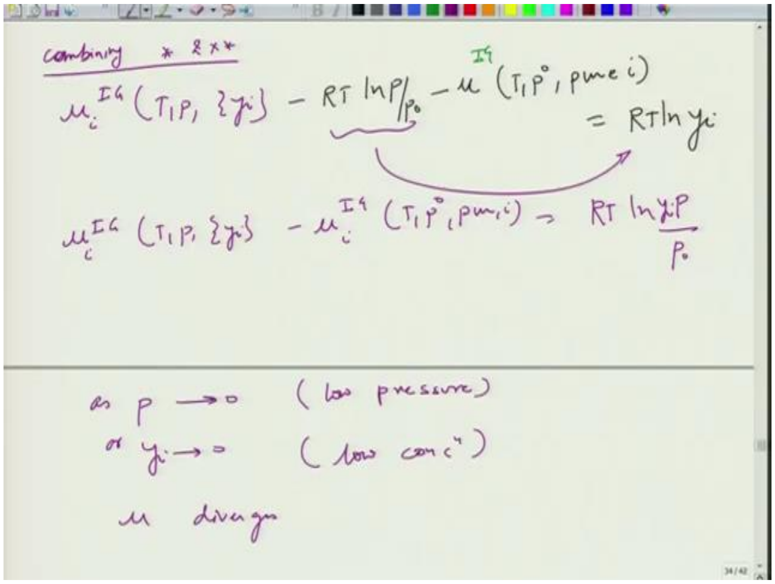

combining * & **

$\mu_i^{IG}(T,P,\{y_i\}) - RT\ln P/P_0 - \mu^{IG}(T,P^0,\text{pure } i) = RT\ln y_i$

$\mu_i^{IG}(T,P,\{y_i\}) - \mu_i^{IG}(T,P^0,\text{pure } i) = RT\ln\frac{y_iP}{P_0}$

as $P \to 0$ (low pressure)

or $y_i \to 0$ (low conc^n)

μ diverges

So, with this we have the expression U IG T, P UI minus U IG T, P0 pure I, okay. But now we have this RT LN P YI times P divided by P0, okay. So that is an expression we have, okay. Now this is, this tells you that the chemical potential of component I here in the mixture with reference to the chemical potential of the pure component at a specific pressure P0 reference pressure that will be equal to RT LN YIP, okay, which is nothing but a partial pressure divided by the reference pressure, okay.

That is what this is basically is telling you this expression. Now this also suggest that as P goes to 0 that means lower pressure or YI goes 0 that is low concentration, so low pressure and this is at low concentration, okay. So, if the equation suggests that as P tends to 0 or YI tends to 0 U diverges, okay, but this the usual the case for ideal gas. So essentially this equation poses the problem numerically because it will divergence you cannot use it effectively.

So, what we do? We would the same thing as we have done that for the case of the pure system, pure fluid. We will introduce a variable which we have done that past is called fugacity.

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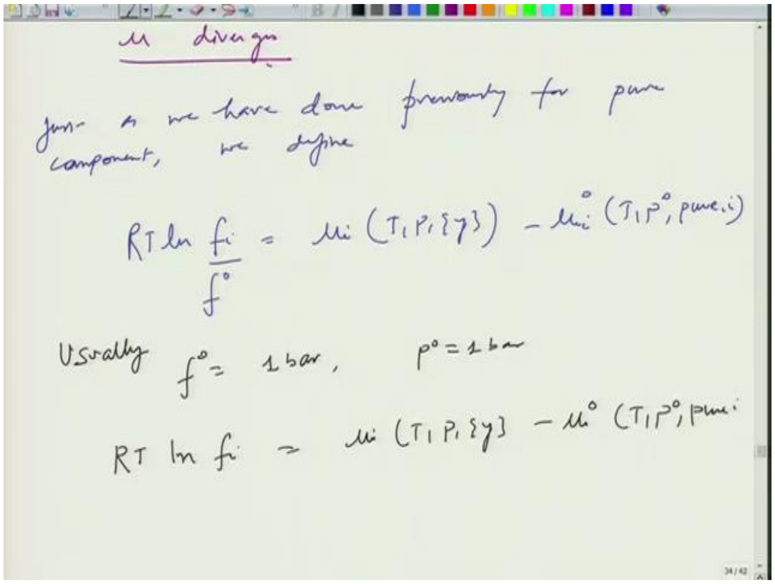

μ diverges

Just as we have done previously for pure component, we define

$$RT \ln \frac{f_i}{f^\circ} = \mu_i (T, P, \{y\}) - \mu_i^\circ (T, P^\circ, pure\ i)$$

Usually $f^\circ = 1\ bar$, $P^\circ = 1\ bar$

$$RT \ln f_i = \mu_i (T, P, \{y\}) - \mu^\circ (T, P^\circ, pure\ i$$

$$RT \ln \frac{f_i}{f^0} = \mu_i(T, P, \{y\}) - \mu_i^0(T, P^0, pure\ i)$$

$$Usually, f^0 = 1\ bar, \qquad P^0 = 1\ bar$$

$$RTln\ f_i = \mu_i(T, P, \{y\}) - \mu_i^0(T, P^0, pure\ i)$$

$$RTln \frac{f_i^1}{f_i^2} = \mu_i(T, P^1, \{y\}) - \mu_i(T, P^2, \{y\})$$

So how we are going to define here? Let me just write it down. So just as we have done previously for pure component, we will define, so we are going to define here RT LN FI by F0. This would your UI T, P Y chemical potential T, P Y minus UI0 T, P0 pure I, okay. So, this a generic definition. So now at this point when I am writing this, I am not saying that this is an ideal gas, okay.

This is to define that the chemical potential difference with reference to reference value is defined as RT LN FU F0, okay. Now here F0 and P0 are related, so once you fix this P0, basically you are fixing F0. So usually F0 is 1 bar at P0 is 1 bar. So, once you say that 1 bar basically you are saying P0 is also 1 bar, okay. So, in that case you can simply write this as RT LN FI is nothing but UI T, P Y minus UI0 T, P0 pure I, okay.

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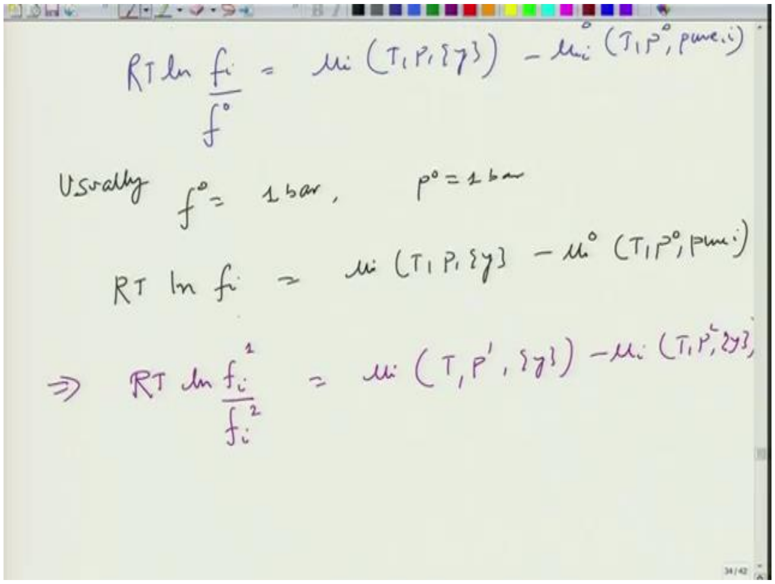

$$RT \ln \frac{f_i}{f^{\circ}} = \mu_i(T, P, \{y\}) - \mu_i^{\circ}(T, P^{\circ}, \text{pure } i)$$

Usually $f^{\circ} = 1 \text{ bar}$, $P^{\circ} = 1 \text{ bar}$

$$RT \ln f_i = \mu_i(T, P, \{y\} - \mu^{\circ}(T, P^{\circ}, \text{pure } i)$$

$$\Rightarrow RT \ln \frac{f_i^1}{f_i^2} = \mu_i(T, P^1, \{y\}) - \mu_i(T, P^2, \{y\},$$

Now if you want to get rid of this reference essentially you would also need another condition, so this would imply also that for another let us say pressure, keeping the temperature fixed you can write this as LN F2 by F1, let me write it again, so this is let us say component, we are talking, still talking about component 1 or some I, so this could be I, this I, but this is let us say 1 this is 2, and what we are talking about is basically T, P1 minus UI T, P2, okay.

So, this is another way to say that if you want to get rid of that. So essentially you are looking at change in the pressure and you are finding the difference between these relations, okay. Because this is just a bit of understanding of the fugacity in this relation, but let us consider specific case.

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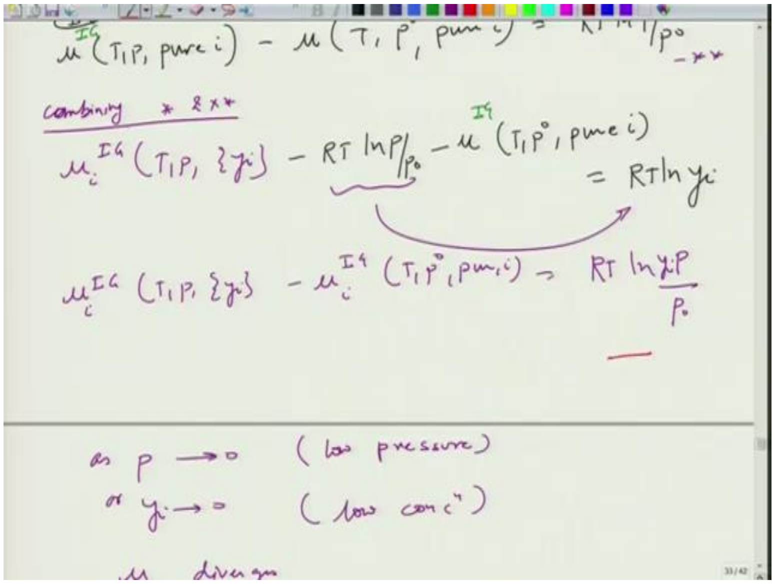

$$\mu^{IG}(T,P,\text{pure } i) - \mu(T,P^{\circ},\text{pure } i) = RT\ln P/P^{\circ} \quad -**$$

combining * & **

$$\mu_i^{IG}(T,P,\{y_i\}) - \underbrace{RT\ln P/P^{\circ}}_{} - \mu^{IG}(T,P^{\circ},\text{pure } i) = RT\ln y_i$$

$$\mu_i^{IG}(T,P,\{y_i\}) - \mu_i^{IG}(T,P^{\circ},\text{pure } i) = RT\ln \frac{y_i P}{P^{\circ}}$$

as $P \to 0$ (low pressure)

or $y_i \to 0$ (low conc^n)

μ diverges

Write about this part, okay. So if you consider this and essentially now consider this for let us say compare this one with the definition of the fugacity, so you use this here and now you compare with the fugacity relation then.

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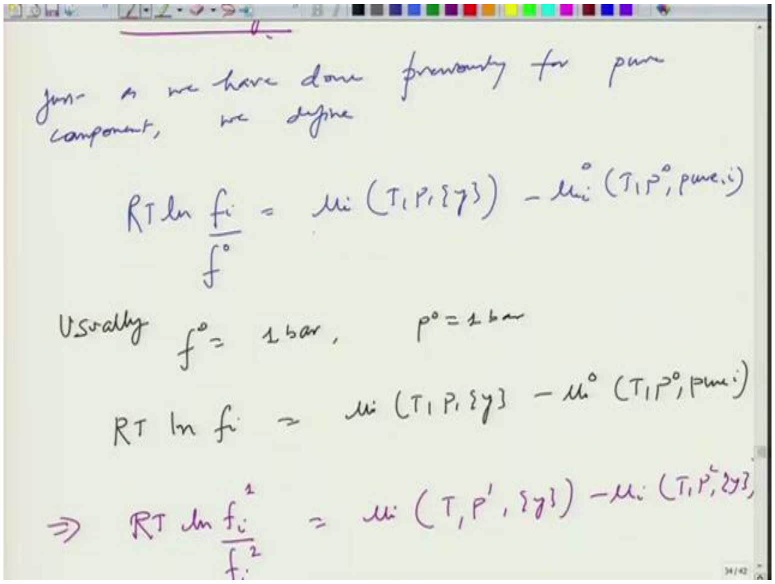

Just as we have done previously for pure component, we define

$$RT\ln\frac{f_i}{f^{\circ}} = \mu_i(T,P,\{y\}) - \mu_i^{\circ}(T,P^{\circ},\text{pure } i)$$

Usually $f^{\circ} = 1$ bar, $P^{\circ} = 1$ bar

$$RT\ln f_i = \mu_i(T,P,\{y\}) - \mu_i^{\circ}(T,P^{\circ},\text{pure } i)$$

$$\Rightarrow RT\ln\frac{f_i^1}{f_i^2} = \mu_i(T,P^1,\{y\}) - \mu_i(T,P^2,\{y\})$$

The following you can easily derive here, so if you look at this, this is the same term but the right hand side, okay, will be you RT LN Y P by P0, that is what we written earlier, right, for the ideal gas.

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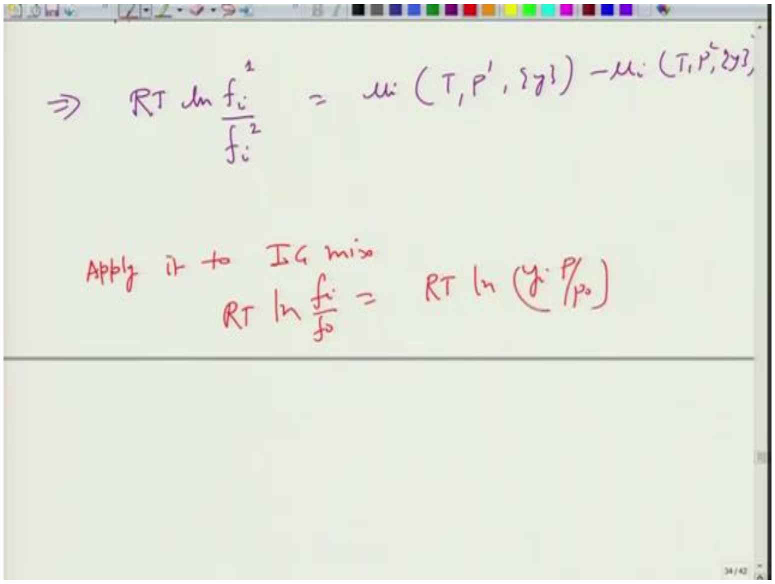

$$\Rightarrow RT \ln \frac{f_i^1}{f_i^2} = \mu_i (T, P^1, \{y\}) - \mu_i (T, P^2, \{y\}$$

Apply it to IG mix

$$RT \ln \frac{f_i}{f_0} = RT \ln \left(y_i P/P_0\right)$$

$$Applying\ to\ IG\ mix: \qquad RTln\frac{f_i}{f_0} = RTln\left(\frac{y_iP}{P_0}\right)$$

So if you just compare this and apply this expression to ideal gas, ideal gas, ideal gas mixture the definition here then you can show that FI by F0, so because is going to be RT LN0, this is nothing but RT LN I P by P0, right. So this is what you can clearly see. If you use this expression and compare this with this expression then essentially you are saying that this right hand side is equal to this, okay, which essentially leads to this expression.

Now this tells you that FI by F0 is nothing but YI P by P0. Now this though we are saying that is ideal gas mixture, we applying the ideal gas mixture, but this particular definition which we have written here does not impose any condition on the phase that gas or liquid, so you can indirectly consider also you extend it to the liquid phase as well.

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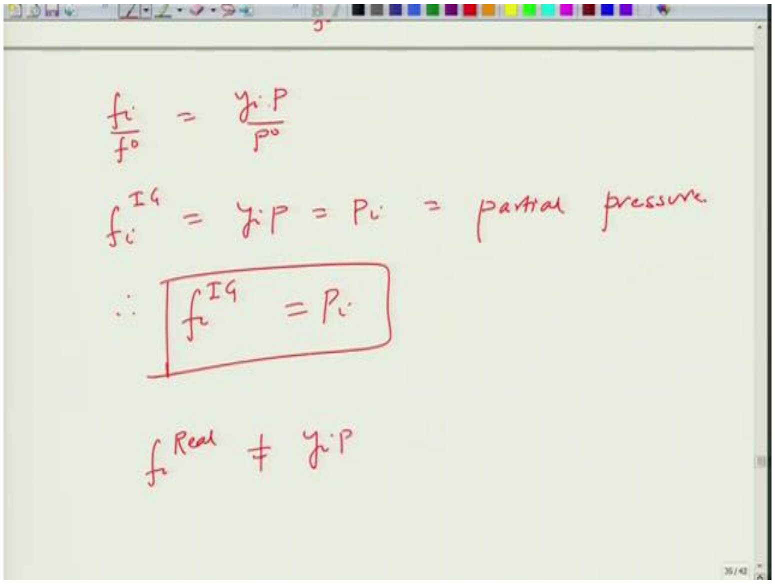

$$\frac{f_i}{f^0} = \frac{y_i P}{P^0}$$

$$f_i^{IG} = y_i P = P_i = \text{partial pressure}$$

$$\therefore \boxed{f_i^{IG} = P_i}$$

$$f_i^{Real} \neq y_i P$$

$$\frac{f_i}{f^0} = \frac{y_i P}{P^0}$$

$$f_i^{IG} = y_i P = P_i = partial\ pressure$$

$$f_i^{IG} = P_i \qquad f_i^{Real} \neq y_i P$$

So, though I am writing here the mole fraction as a Y which is usually consider for the gas phase, but this could be a liquid phase also, okay. But of course, we will be mostly using for the gas phase here. So let us look at it here. So if you consider this conscience F0 and P0 are connected, I can simply write FI, this is now for the ideal gas is nothing but YI P, YI P is nothing but PI, okay.

So therefore, FI of ideal gas, fugacity of the component I in the ideal gas mixture is nothing but the partial pressure, okay. So what about the real fluids or real gas, so certainly real gas will not be equal to YI previous, right.

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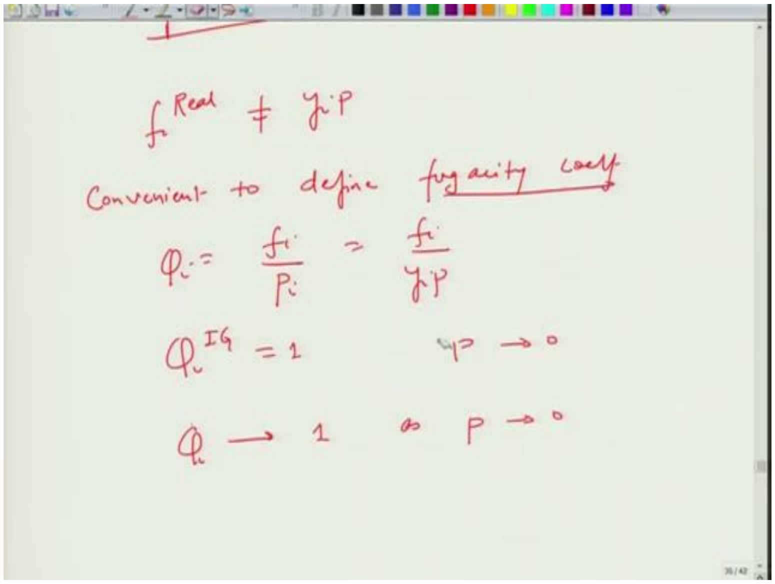

$f_i^{Real} \neq y_i P$

Convenient to define fugacity coeff

$\phi_i = \frac{f_i}{P_i} = \frac{f_i}{y_i P}$

$\phi_i^{IG} = 1 \quad y_i P \to 0$

$\phi_i \to 1 \quad as \quad P \to 0$

$$\phi_i = \frac{f_i}{P_i} = \frac{f_i}{y_i P}$$

$$\phi_i^{IG} = 1 \quad P \to 0$$

$$\phi_i \to 1 \quad as\ P \to 0$$

And only at specific conditions when this, the fluid behaves like ideal gas, you will have FI real fluid behaving like an ideal gas then it will have the FI value to be the partial pressure. So in order to define the deviation or in order to observe the deviation from the ideal gas, we can define a very convenient parameter which we called it a fugacity coefficient, okay. So it is convenient to define a fugacity coefficient because this can identify the deviation from ideal gas, so ideal gas, so what we can use, we can use this ratio of this FI IG and PI, so we can say that FI by PI or FI by YIP.

So this ratio will be called as a fugacity coefficient. So naturally for the case of ideal gas, this is 1, but otherwise it is not. This will happen only when the pressure approaches to 0. So that means basically all the FI in general will approach towards 1 as P approach towards 0, right. Okay, so that is something which is which wanted to discuss at this point where we started with a basically the relations of the chemical potentials with the mole fractions in the binary, in ideal gas mixtures and we started from the derivative of delta G ideal gas mixture, okay.

And then we have derived this expression, okay. And then we said well, the problem comes in when we use this pressure and see that the pressure itself and it goes to 0 this equation diverges and then we recall that we have done this exercise in the pure phase where we have tried to use fugacity as a mean to avoid this kind of divergence of the chemical potentials at a very low pressure.

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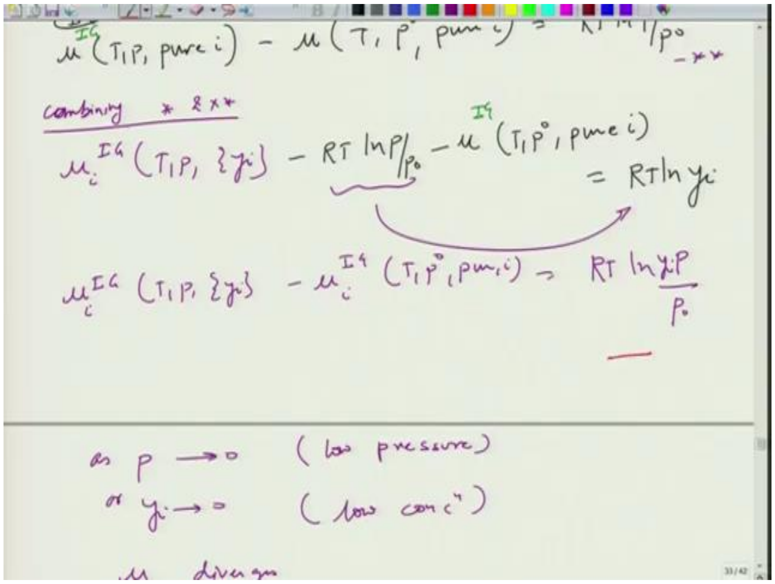

$$\mu^{IG}(T,P,\text{pure } i) - \mu(T,P^\circ,\text{pure } i) = RT\ln P/P^\circ \quad -{*}{*}$$

combining * & **

$$\mu_i^{IG}(T,P,\{y_i\}) - \underbrace{RT\ln P/P^\circ}_{} - \mu^{IG}(T,P^\circ,\text{pure } i) = RT\ln y_i$$

$$\mu_i^{IG}(T,P,\{y_i\}) - \mu_i^{IG}(T,P^\circ,\text{pure } i) = RT\ln \frac{y_iP}{P^\circ}$$

as $P \rightarrow 0$ (low pressure)

or $y_i \rightarrow 0$ (low conc^n)

μ diverges

So we have used that fugacity here as well, now we use that expression and connected the fugacity in the gas phase mixtures to the mole fractions and the pressure. And particularly for ideal gas, the fugacity of a component I is nothing but the partial pressure. So for that in order to find out the deviation from the ideal gas, we defined a term which we called fugacity coefficient

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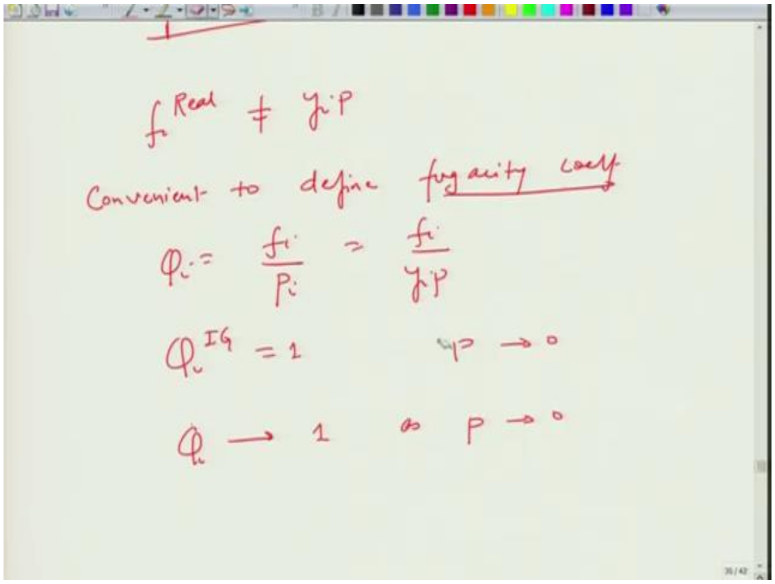

$f_i^{Real} \neq y_i P$

Convenient to define fugacity coeff

$\phi_i = \frac{f_i}{P_i} = \frac{f_i}{y_i P}$

$\phi_i^{IG} = 1 \qquad y_i P \to 0$

$\phi_i \to 1$ as $P \to 0$

So something which is straight forward at this point. Now the question is, how do we find out this fugacity coefficient when you have volumetric data is all equational state available? so this is, these are the two specific question which we need to address, okay.

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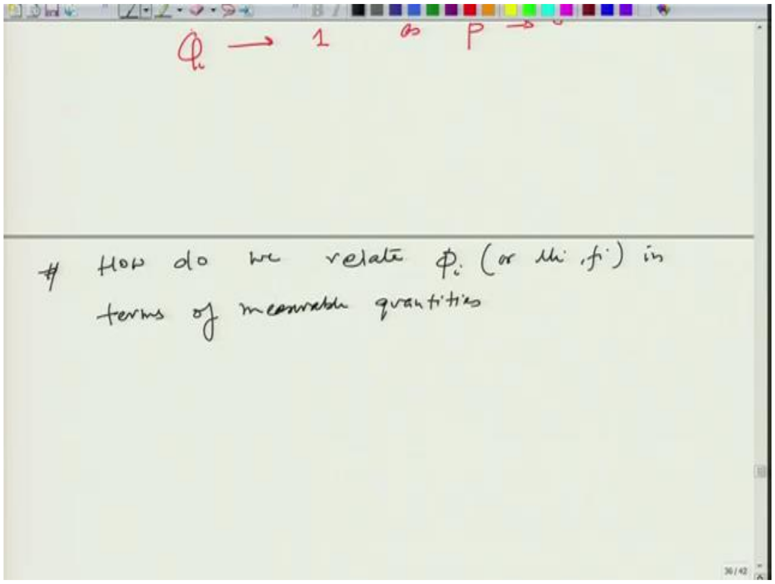

$\phi_i \to 1$ as $P \to 0$

How do we relate ϕ_i (or μ_i, f_i) in terms of measurable quantities

So let me just work on this, so the question is now, how do we relate PI, right, and if you are talking about PI, you are also talking about UI, FI, okay, in terms of measurable quantities.

So this the basically the key question at this point and once you are able to derive this and understand it then essentially we can make use of whether the experimental data is available or whether the equation states are known, using that information, we should be able to find out PI. We also talking about the relevance of PI.

When we try to address the questions of the phase equilibria, okay, as subsequently we all also understand how do we relate this deviation from the ideal gas mixtures in terms of other properties also. So I think we are almost there to understand completely of the gas phase mixtures and subsequently we will take a liquid mixtures, but this particular question of, how do we relate PI in terms of measurable quantities? I will describe in length in the next lecture, okay. So now I will close it. I will take it up again, so I will see you next time.