Course on Phase Equilibrium Thermodynamics
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Lecture No 35
Partial Molar Fugacity

Well, in the last class we had started discussing the characteristics of mixtures and then we found out that in order to properly define mixture properties in terms of single phase or rather the pure component properties we had to propose a number of mixing rules and combining rules whether we were using the cubic equation of state, the Virial equation of state or the compressibility factor charts.

So we have to propose a number of mixing rules which gave us the constants characteristics of the mixture in terms of the pure component constants and then we found out that in those particular this empirical laws there were some interaction parameters which took into account the interaction between unlike molecules and in order to express them in terms of interactions between light molecules say for example there is a mixture constituting of component a and component b.

We would like to express the interaction of component a and b in terms of the interactions between molecules of component a and the molecules of component b.

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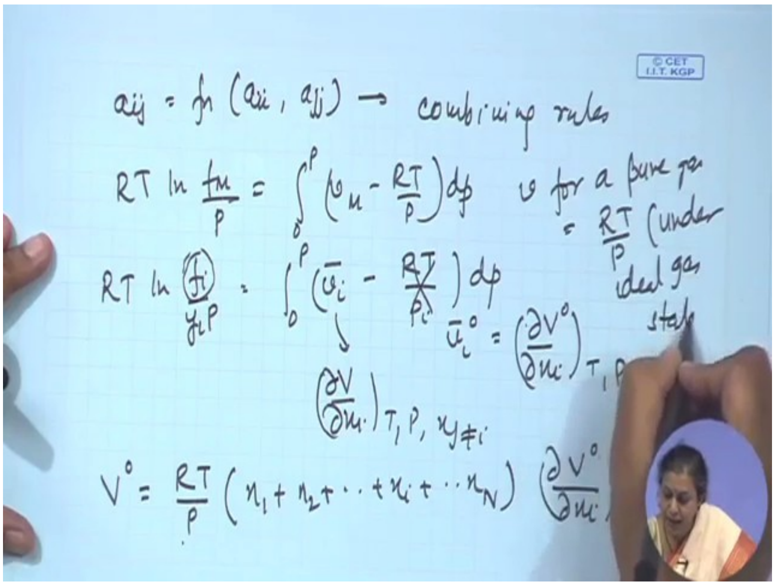

$a_{ij} = fn(a_{ii}, a_{jj}) \rightarrow$ combining rules

$RT \ln \frac{f_M}{P} = \int_0^P \left(v_M - \frac{RT}{P}\right) dp$ $\quad v$ for a pure gas $= \frac{RT}{P}$ (under ideal gas state

$RT \ln \frac{\hat{f}_i}{y_i P} = \int_0^P \left(\bar{v}_i - \frac{RT}{\cancel{P_i}}\right) dp$

$\bar{v}_i \rightarrow \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_{j \neq i}}$

$\bar{v}_i^0 = \left(\frac{\partial V^0}{\partial n_i}\right)_{T, P}$

$V^0 = \frac{RT}{P}(n_1 + n_2 + \cdots + n_i + \cdots n_N)$ $\quad \left(\frac{\partial V^0}{\partial n_i}\right)$

So in other words we would like to express aij in terms of aii and ajj and this was possible by means of combining rules so we have devised a number of combining and mixing rules and based on those we had tried to define the mixture properties in terms of the pure common properties.

And then we found out that suppose we would like to define particularly fugacity of a component i in a mixture of say c number of components where i extends from 1 to c then in that case and I had also explained why it is so very important to define the fugacity of component i in a mixture because that is what decides the phase equilibrium conditions. Now under that conditions we have found out from the basic equation RT ln 0 to Pv mixture minus RT by P dp this was for the mixture case.

Now if I try to find out the fugacity of component i in the mixture, so therefore what does it become? It becomes fi which is actually the partial mole or the contribution of component i to the mixture product. So normally for any and this should be I will be explaining all the terms this should be 0 to P and here it should be vi bar where vi bar it is nothing but I had already described it was del V del ni at constant TP nj not equals to i minus we are often tempted to write this down as minus RT by Pi.

We are tempted to write it in this particular form. Now let us see what should be here and what should be here before we proceed? Now what from where did this term come? This term is actually vi bar 0 what does it mean? It means the partial molar volume of component i in the ideal gas mixture, a mixture of ideal gases there what is this vi bar0? Now what is this equals to? This should be equal to del v del ni where this is for the ideal gas TP nj not equal to i, right?

Now what is the total volume of the mixture? Total volume is RT by P into n1 plus n2 say nith component it was still nN component, right? Now suppose I differentiate this with respect to component ni, what do I get? I get del V0 del ni at constant T is constant P is constant all other mole numbers are constant. So therefore what does it reduce to? I can just get this one differential term when I am differentiating it with respect to ni RT by P where all other terms they cancel out.

So therefore under that condition this reduces to RT by P. So therefore it is very important to remember that basically the term which I use here it is the partial molar volume of any particular component i in this case this RT by P came because it was the volume of the total gas mixture in the ideal gas state because it is important to remember that whenever I define fugacity it is with respect to P equals to 0 where the gas behaves as an ideal gas and therefore it is important to remember that v for the molar volume for a pure gas or a single component gas that is equal to RT by P under ideal gas state, right?

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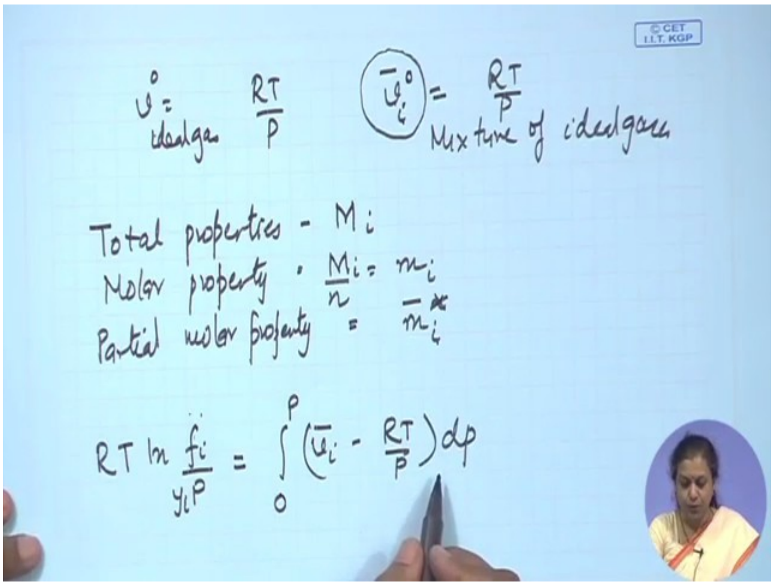

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$v^{0}_{\text{ideal gas}} = \frac{RT}{P}$ $\quad \boxed{\bar{v}_i^{0}} = \frac{RT}{P}$ Mixture of ideal gases

Total properties - M_i

Molar property : $\frac{M_i}{n} = m_i$

Partial molar property = $\bar{m}_i^{*}$

$$RT \ln \frac{\hat{f}_i}{y_i P} = \int_0^P \left(\bar{v}_i - \frac{RT}{P} \right) dp$$

In the same way, so I will just repeat it once more in the same way v for an v0 ideal gas naturally 0 means ideal gas that is equal to RT by P. Interestingly suppose this same gas it is in a mixture with other gases where I have to define the partial molar volume just note the partial molar volume since it is molar it is small case it refers to component i subscript i, it refers to the ideal gas state superscript 0 this is a partial molar volume there is a bar.

So just remember if unless you give all the notations all the necessary details are provided in this particular nomenclature if you miss any of them then the notation becomes incomplete. So therefore I keep on emphasizing the importance of correct depiction of different properties. Again I repeat the primary reason for this is that we are using or rather we will be dealing with a host of different sets of properties just for your convenience if I can write it down total properties that means properties for the entire mass or for the whole system they are given in terms of capital M.

Molar property the corresponding molar property it is nothing but the total property divided by the number of moles contained in that particular component whether it is a mixture whether it is a pure substance whatever it is this will be denoted by m. Next we go for partial molar properties these have meaning only when any component i, suppose the total properties for component i, so I can write it down as Mi this is Mi this is mi, okay.

Now when this component i is dissolved in a solution with other components then only the partial molar property comes into being otherwise no. So therefore when it comes what is this? This is a molar property small case, molar property of what; i suppose it would have been in a phase Alpha. Suppose I have 2 phases each comprising of say n components of n components of pure substance say in phase Alpha n components of pure components in say phase beta.

Then in that case the partial molar property of component i in the Alpha phase would have been shown in this particular form. Suppose if I had 2 phases but at the moment since we are dealing with just mixtures either in say the vapor phase or in the liquid phase so for the time being I am not mentioning this but moment we are going to mention phases and components please remember component is subscript, phase is superscript and small case means molar and bar means partial molar property, right?

So therefore the partial molar property of component i in the ideal gas state that is when suppose I assume that the gas mixture which I have is a mixture of ideal gases, for that particular case I find for a mixture of ideal gases this is also equals to RT by P very frequently written to confuse this therefore it is very important to remember. So therefore accordingly what is the equation for finding out the fugacity? It is RT ln the fugacity how I am going to denote this fugacity? We are going to discuss.

Normally if we feel that they are there should be a bar but whether I would give a bar here on something else that I will be discussing a little later. And this fugacity it has to be expressed in terms of the fugacity of this particular component i in the ideal gas state. What is the fugacity of this particular component i in the ideal gas state? If this i would have remained as a pure component than the fugacity would have been equal to the pressure in the ideal gas state but when it is mixed with a large number of components then it manifests itself as the partial pressure of component i in the gas phase.

So therefore this gives us the fugacity of component i in any particular state other than the ideal gas state and therefore in order to find this out what do I need? I need to integrate it from very low pressure under which this particular real gas behaves as an ideal gas and the fugacity it is the partial pressure from this state to the pressure P where we normally wanted and this is equals to vi bar minus vi bar 0 which is nothing but equal to RT by P dp. So till this much we have defined in the last class.

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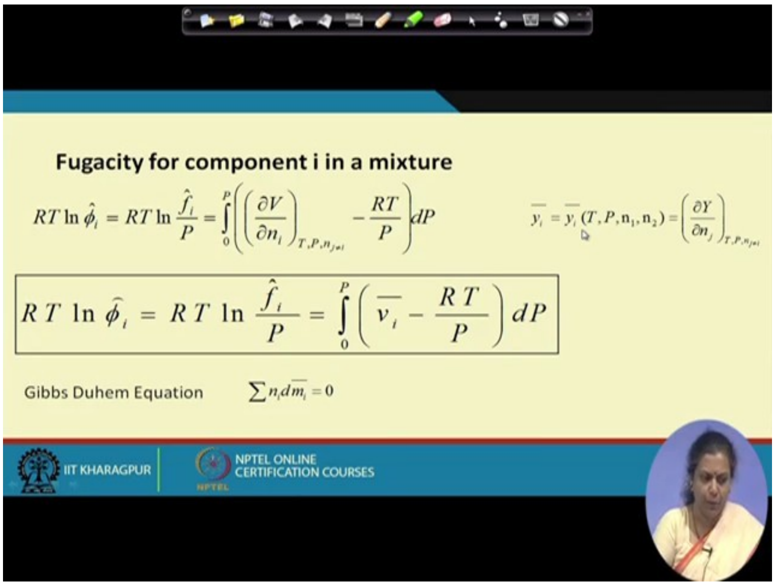

Fugacity for component i in a mixture

$$RT\ln\hat{\phi}_i = RT\ln\frac{\hat{f}_i}{P} = \int_0^P\left(\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} - \frac{RT}{P}\right)dP \qquad \overline{y_i} = \overline{y_i}(T,P,n_1,n_2) = \left(\frac{\partial Y}{\partial n_j}\right)_{T,P,n_{j\neq i}}$$

$$\boxed{RT\ln\hat{\phi}_i = RT\ln\frac{\hat{f}_i}{P} = \int_0^P\left(\overline{v_i} - \frac{RT}{P}\right)dP}$$

Gibbs Duhem Equation $\sum n_i d\overline{m_i} = 0$

I have also noted this down here with a proper definition of partial molar properties. Now when we go to find this then what did we find?

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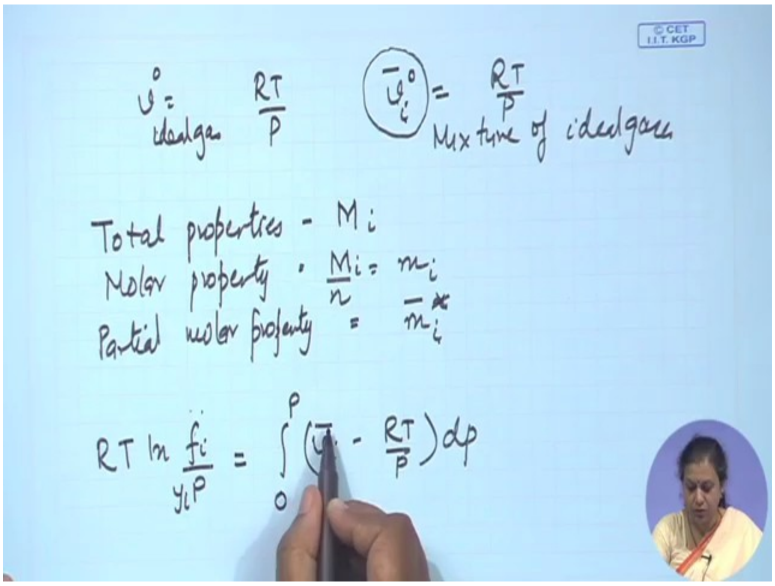

$v^0_{\text{ideal gas}} = \frac{RT}{P}$ $\boxed{\bar{v}_i^0} = \frac{RT}{P}$ Mixture of ideal gases

Total properties - M_i

Molar property : $\frac{M_i}{n} = m_i$

Partial molar property = $\bar{m}_i^*$

$$RT\ln\frac{\hat{f}_i}{y_i P} = \int_0^P\left(\bar{v}_i - \frac{RT}{P}\right)dp$$

That in order to calculate fugacity we need to know the partial molar volume of component i in the mixture not only at the pressure of interest but since it is inside the integral we need to know this particular value or how this varies with pressure right from P equals to 0 to the pressure of interest, right?

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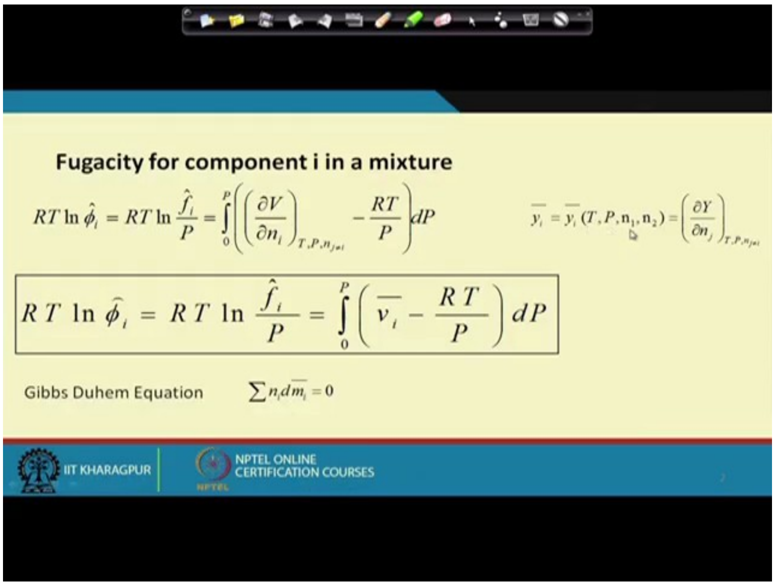

Fugacity for component i in a mixture

$$RT\ln\hat{\phi}_i = RT\ln\frac{\hat{f}_i}{P} = \int_0^P\left(\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} - \frac{RT}{P}\right)dP \qquad \overline{y_i} = \overline{y_i}(T,P,n_1,n_2) = \left(\frac{\partial Y}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

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Gibbs Duhem Equation $\sum n_i d\overline{m_i} = 0$

So we need to know the partial molar volume and also what is the other thing we know which I have already mentioned here?

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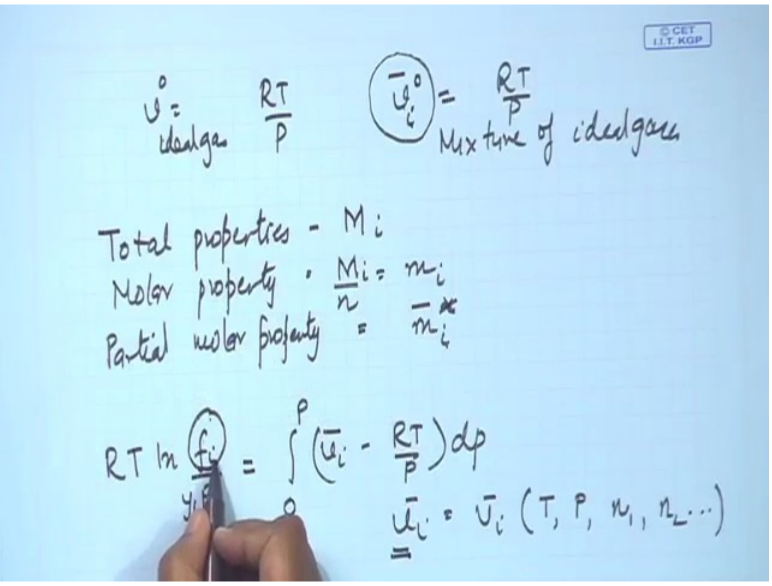

$\overset{\circ}{v} = \frac{RT}{P}$ idealgas $\qquad \boxed{\overline{v}_i^{\circ}} = \frac{RT}{P}$ Mixture of idealgases

Total properties - M_i

Molar property . $\frac{M_i}{n} = m_i$

Partial molar property $= \overline{m}_i^*$

$RT\ln\frac{\boxed{f_i}}{y_i P} = \int_0^P\left(\overline{v}_i - \frac{RT}{P}\right)dp$

$\underline{\underline{\overline{v}_i}} = \overline{v}_i(T, P, n_1, n_2 \ldots)$

The partial molar volume it is not only a function of this will be a function of temperature that we can keep constant the total pressure and it will be a function of the mole numbers of all the components or in other words it's a function of composition we had already seen in the last class that this is different for different compositions of the same set of components making up the mixture and it is also important and the composition it depends upon the nature of the or molecules of component i.

It is dependent upon the nature of the other molecules which are present, so therefore finding vi bar in terms of P over the entire integration from 0 to P that is something very difficult in any case we had already discussed that even finding out a generalized equation of state even for a pure component over a large range of conditions comprising the 2 phases was anyhow difficult and we have already got a favour of the large variety and number of equations that we deal in order to describe the PVT behaviour of gases.

The tremendous number of equations which had come up as I had already mentioned was just because no one equation was found to be suitable for the entire range of conditions that we would be dealing, right? So therefore in this particular case also it was quite difficult. So naturally what people then tried to do? People then tried to find out whether any particular simplified model can be used in order to calculate the partial molar fugacity of component i in the mixture before we go that it is important for us to realize the unique position of the fugacity of component i in the mixture as distinguishing from the partial molar property of any other compound for any other component.

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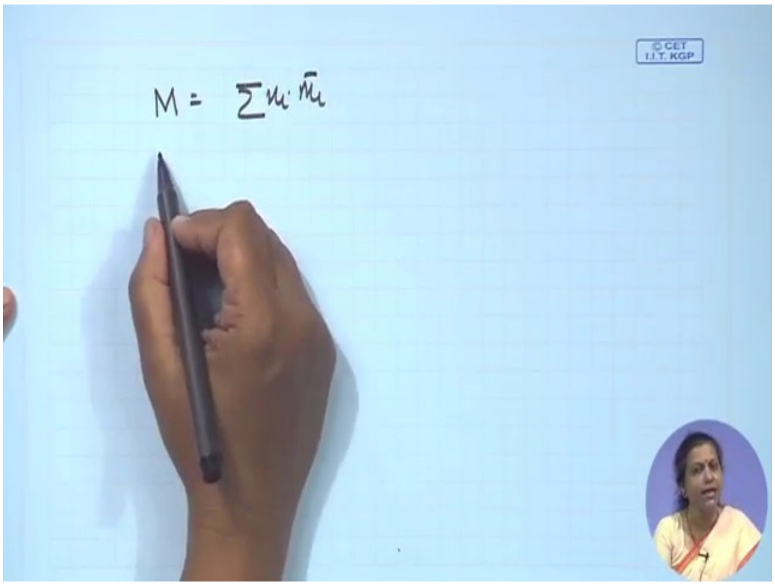

$$M = \sum n_i \bar{m}_i$$

For any other component what did we find? We found out that partial molar properties they are additive in nature or in other words when I write the total property it is nothing but equal to ni mi bar where m is an extensive property and in terms of molar property we can write xi mi bar that we have already seen, okay. We had tried to express it in terms of volume, enthalpy, entropy everything what about partial molar fugacity?

Let us see how the fugacity of the mixture in what way is it related to the fugacity of component i in the mixture. Does it obey do we have a relation like fM equals to xi say fi bar or something of component i in the mixture. Do we really have such a equation? Or such an equation does not hold for fM, let us for everything that we do we are going to start from the basics.

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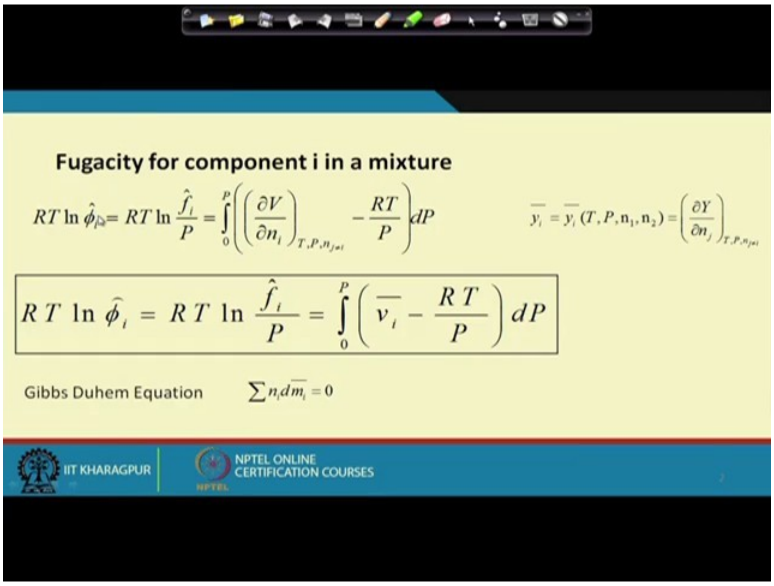

Fugacity for component i in a mixture

$$RT\ln\hat{\phi}_i = RT\ln\frac{\hat{f}_i}{P} = \int_0^P\left(\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} - \frac{RT}{P}\right)dP$$

$$\overline{y_i} = \overline{y_i}(T,P,n_1,n_2) = \left(\frac{\partial Y}{\partial n_j}\right)_{T,P,n_{j\neq i}}$$

$$\boxed{RT\ln\hat{\phi}_i = RT\ln\frac{\hat{f}_i}{P} = \int_0^P\left(\overline{v_i} - \frac{RT}{P}\right)dP}$$

Gibbs Duhem Equation $\sum n_i d\overline{m_i} = 0$

This is very important because we have to start everywhere everything that we do this is the basic equation from which we are going to start why? Because moment you try to jump steps you will find that with standards states etc you are going to get completely confused, right? So therefore this is something very important and so therefore let us see what we can do about it. So therefore let us start from the very basic equation which is given by this particular form.

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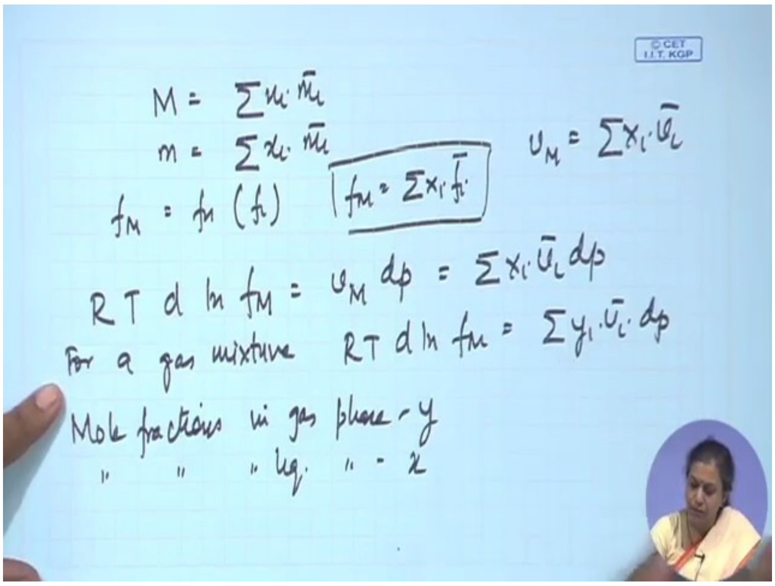

$M = \sum x_i \cdot \bar{m}_i$

$m = \sum x_i \cdot \bar{m}_i$

$f_M = fn\,(f_i)$ $\quad \boxed{f_M = \sum x_i \bar{f}_i} \quad$ $v_M = \sum x_i \cdot \bar{v}_i$

$RT\, d \ln f_M = v_M\, dp = \sum x_i \cdot \bar{v}_i\, dp$

For a gas mixture $RT\, d \ln f_M = \sum y_i \cdot \bar{v}_i \cdot dp$

Mole fractions in gas phase - y

" " " liq. " - x

Now what is that equation? What is the basic defining equation RT d ln fM which is the fugacity of the total mixture that is equal to vM dp, right? This one we know. What is vM equals to? Just if we can write it in this particular terms v mixture is nothing but Sigma xi vi bar, fine. So instead of vM can I not write it down at as xivi bar dp, fine.

Or suppose for a gas mixture suppose because usually we will deal with gases and then we will come to liquid in that particular case RT d ln fM, normally again let me define that mole fractions this is another definition which you need to know mole fractions in gas phase they will be denoted by y mole fractions in the liquid phase will be denoted by x, right? So therefore what do we find? That the relationship between d ln fM with a partial molar volume is given in this particular form, now suppose I try to expand it then what do I get?

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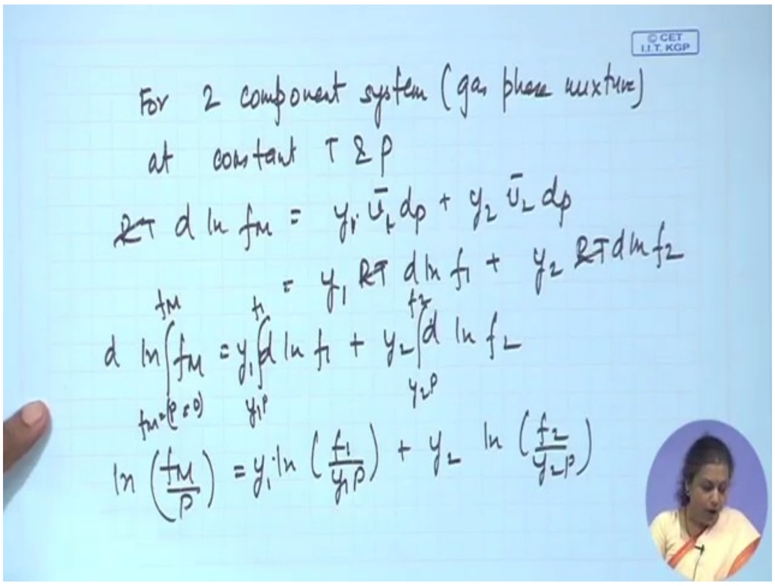

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For 2 component system (gas phase mixture)

at constant T & P

$$\cancel{RT}\, d \ln f_M = y_1 \bar{v}_1 dp + y_2 \bar{v}_2 dp$$

$$= y_1 RT\, d \ln f_1 + y_2 \cancel{RT}\, d \ln f_2$$

$$d \ln \int_{f_M = P(P=0)}^{f_M} f_M = y_1 \int_{y_1 P}^{f_1} d \ln f_1 + y_2 \int_{y_2 P}^{f_2} d \ln f_2$$

$$\ln \left(\frac{f_M}{P}\right) = y_1 \ln \left(\frac{f_1}{y_1 P}\right) + y_2 \ln \left(\frac{f_2}{y_2 P}\right)$$

Say for the time being just for simplicity for 2 component system which is gas phase mixture at constant temperature and pressure. If I elaborate that what do I get? RT d ln fM this is equals to y1v1 bar dp plus y2v2 bar dp, agreed?

Now what is this y v1 bar dp can you tell me? This v1 bar dp it was nothing but y1 RT d ln f1, agreed? Which is the partial molar fugacity of component 1 in the mixture plus y2 RT d ln f2, the RT if they cancel out what do we get? We get d ln fM is nothing but y1d ln f1 plus y2 d ln f2, now we start integrating this. If we integrate this from say P equals to 0 where fM equals to P to the point of P of interest where they for P equals to 0 to the point of interest at P.

Definitely we will also be rather we will also be integrating these particular terms also this will be in terms of y1P to some particular situation f1 this will be y2P to say f2. So in that particular case on integration what do we get? We get ln fM by P equals to ln f1 by y1P y1 plus y2 ln f2 by y2P.

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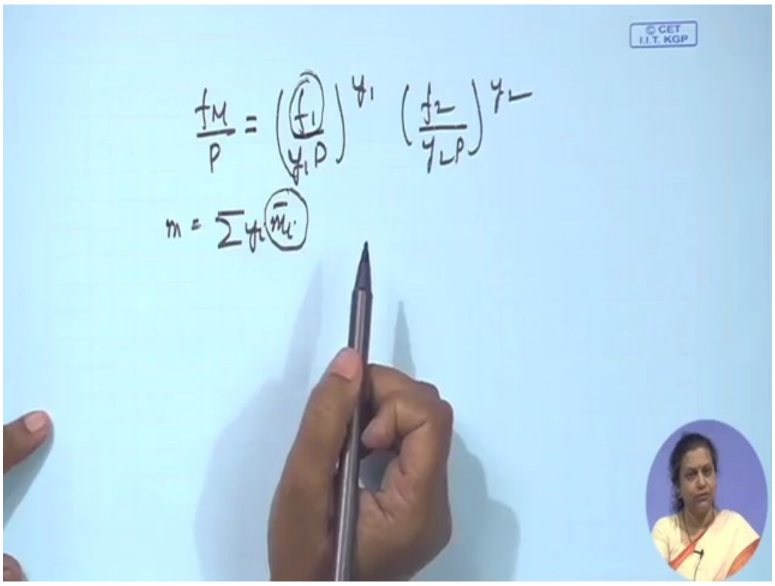

Or in other words for removing the ln terms what do we get? We get fM by P this is equal to f1 by y1 P whole to the power y1 f2 by y2 P whole to the power y2, is it clear to you?

So therefore what is the relationship between partial molar between the fugacity of the mixture and the partial molar fugacity of the individual components it is in no way related to the way the any other partial molar property m is related like yi mi bar so this relation does not hold for the molar fugacity and since it does not hold it is very important to distinguish the partial molar fugacity from any other molar properties.

So what do we do for this? Just to keep on reminding us that the partial molar fugacity does not causes the properties of other partial molar properties it is something different from them, how do we do? We do not denote this with a bar that we have been doing it we denote this with the cap it just a hat to mark that this is different from this.

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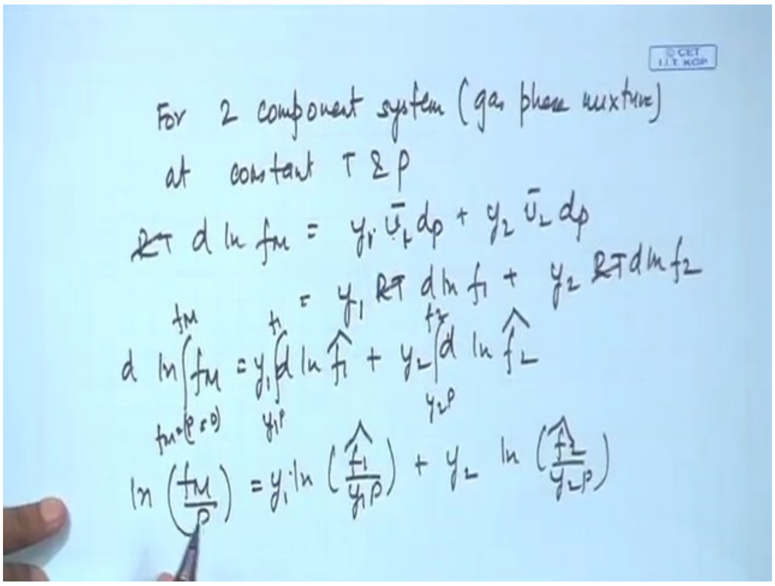

For 2 component system (gas phase mixture)
at constant T & P

$$RT\, d\ln f_M = y_1 \bar{v}_1\, dp + y_2 \bar{v}_2\, dp$$

$$= y_1 RT\, d\ln f_1 + y_2 RT\, d\ln f_2$$

$$\int_{f_M(P=0)}^{f_M} d\ln f_M = y_1 \int_{y_1 P}^{f_1} d\ln \hat{f}_1 + y_2 \int_{y_2 P}^{f_2} d\ln \hat{f}_2$$

$$\ln\left(\frac{f_M}{P}\right) = y_1 \ln\left(\frac{\hat{f}_1}{y_1 P}\right) + y_2 \ln\left(\frac{\hat{f}_2}{y_2 P}\right)$$

So therefore what we do for each partial molar fugacity it is important that we denote them with a cap while we are denoting the partial molar volumes with a bar.

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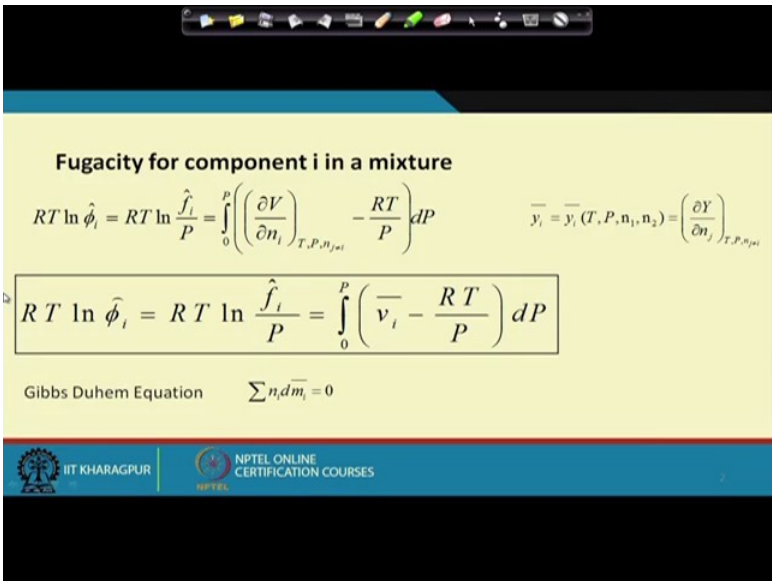

Fugacity for component i in a mixture

$$RT \ln \hat{\phi}_i = RT \ln \frac{\hat{f}_i}{P} = \int_0^P \left(\left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_{j \neq i}} - \frac{RT}{P} \right) dP \qquad \overline{y_i} = \overline{y_i}(T, P, n_1, n_2) = \left(\frac{\partial Y}{\partial n_j} \right)_{T,P,n_{j \neq i}}$$

$$\boxed{RT \ln \hat{\phi}_i = RT \ln \frac{\hat{f}_i}{P} = \int_0^P \left(\overline{v_i} - \frac{RT}{P} \right) dP}$$

Gibbs Duhem Equation $\sum n_i d\overline{m_i} = 0$

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So therefore from this particular equation from this particular equation what are the things that we see? We see from this equation that more or less the fugacity of component i in a mixture it is something different from the fugacities of or rather it is different from the other partial molar volumes number 1.

And also it is important to remember that the molar volume of component i in pure state is equal to the partial molar volume of component i in the mixture. So with this finally what we have done we had tried to define the partial molar fugacity in terms of PvT behaviour of gases when the component i is in a mixture and from there we have realized that since it is very difficult to find out the partial molar volume of component i in mixture not only at the pressure of interest but over the entire range of pressure from 0 to P. So therefore it was felt necessary to suggest or to devise a simpler way of trying to estimate the partial molar fugacity of component i when it is in a mixture.

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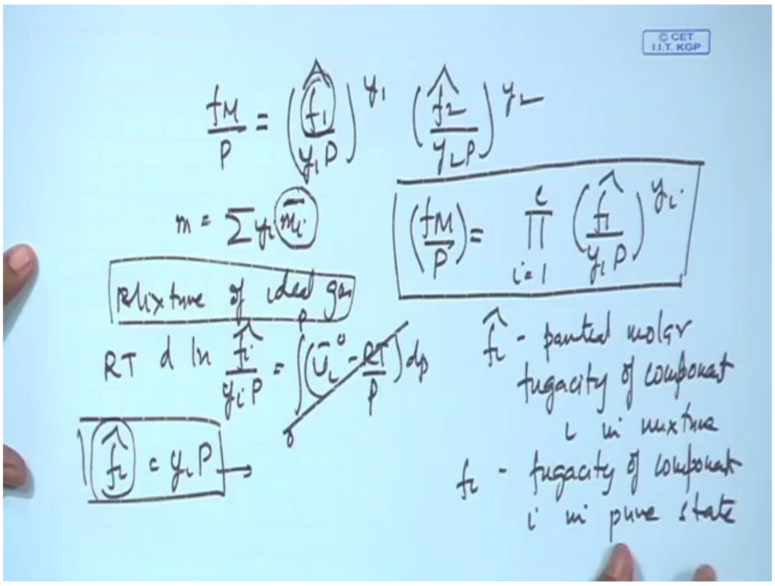

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$$\frac{f_M}{P} = \left(\frac{\hat{f}_1}{y_1 P}\right)^{y_1} \left(\frac{\hat{f}_2}{y_2 P}\right)^{y_2}$$

$$m = \sum y_i \bar{m}_i$$

$$\boxed{\left(\frac{f_M}{P}\right) = \prod_{i=1}^{c} \left(\frac{\hat{f}_i}{y_i P}\right)^{y_i}}$$

Mixture of ideal gas

$$\cancel{RT\, d \ln \frac{\hat{f}_i}{y_i P} = \int_0^P \left(\bar{v}_i^0 - \frac{RT}{P}\right) dp}$$

$$\boxed{\hat{f}_i = y_i P} \rightarrow$$

$\hat{f}_i$ - partial molar fugacity of component i in mixture

f_i - fugacity of component i in pure state

Now how to go about this? What people found out was that they started with gaseous mixtures, in gaseous mixtures what did we find? In gaseous mixtures we observed that again suppose I start writing for gaseous mixtures what do I get? First let me generalize this, so therefore this fM by P it can be better written as not Sigma but product of over i equals to 1 to c fi by yiP whole to the power yi this is something which is quite interesting and quite different.

So the next thing is in order to find out rather since it is very difficult to or rather although it is an exact equation but it is very difficult to find out fi bar, so we wanted to find out some other way by which we can find out fi for the different phases and then we can start solving the other phase equilibrium problems. Now for that what did we take up? We tried to find out something simplifying something much simpler.

So what is the simplest thing that comes to our mind? The simplest thing which comes to our mind is the as I had mentioned mixture of ideal gases. Now there what we have already seen suppose we are dealing with a mixture of ideal gases then in that case again suppose what do

I find? This is nothing but equal to RT d ln now very confidently I will be putting a cap and please do not forget the cap because this just shows the partial molar fugacity here I would like to mention once more that when I put a cap this is partial molar fugacity of component i in mixture and when I just mention fi it is the fugacity of component i in pure state.

So you will find in several textbooks they try to put a 0, a star and lot of things just to make matters simple I am not going to add up anything when it is a partial molar property it has a cap, when it is in a pure state it has no cap and therefore the only thing which and the subscript i it denotes component i, right? So for a mixture of ideal gases what do we find? We find for a mixture of ideal gases this is equal to vi bar minus RT by P the standard equation from 0 to P.

Now when we are dealing with ideal gases then we know this is vi0 which is nothing but equal to RT by P. So for a mixture of ideal gases this term cancels out and we know fi equals to yiP, right? But this is a very restrictive assumption or rather it cannot be generalized very easily, why? Because this assumes that there is no interaction between the molecules.

Now while this can be imagined or this can be accepted for gaseous mixtures we would like to propose a generalized expression to calculate the partial molar fugacity in terms of your compositions or something for all types of solutions be it liquid solution, solid solutions, gaseous solutions everything, right? So therefore using the idealization for the mixture of ideal gases will become too restrictive.

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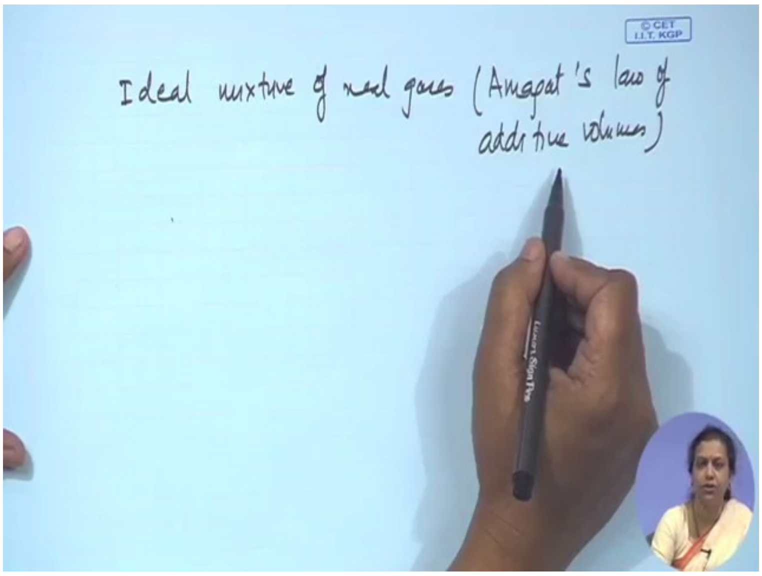

Ideal mixture of real gases (Amagat's law of additive volumes)

Than what people thought or tried to do they tried to find out the situation for an ideal mixture of real gases whether this could be a slightly more generalized portion while being quite simple.

Now generally we find that the ideal mixture of real gases are those which confirm to the Amagat’s law of additive volumes, right? So in the next class we will be dealing with the Amagat’s law of additive volumes and whether it gives us a much more simplified version of calculating the partial molar fugacity in terms of composition, we continue in the next class.