### Course on Phase Equilibrium Thermodynamics

## By Professor Gargi Das
## Department of Chemical Engineering
## Indian Institute of Technology Kharagpur
## Lecture 31
# Mixtures (Contd.)

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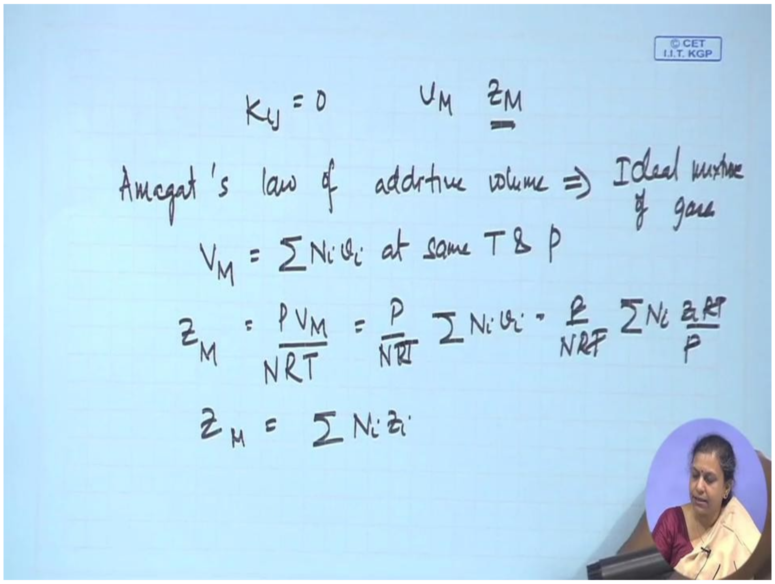

$k_{ij} = 0 \qquad v_M \quad \underline{z_M}$

Amagat's law of additive volume ⇒ Ideal mixture of gases

$V_M = \sum N_i v_i$ at same T & P

$$z_M = \frac{PV_M}{NRT} = \frac{P}{NRT}\sum N_i v_i = \frac{P}{NRT}\sum N_i \frac{z_i RT}{P}$$

$$z_M = \sum N_i z_i$$

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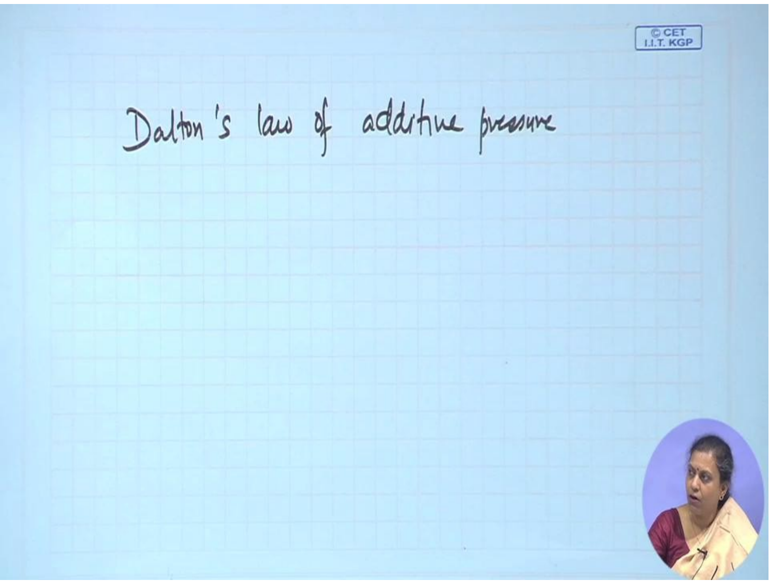

Dalton's law of additive pressure

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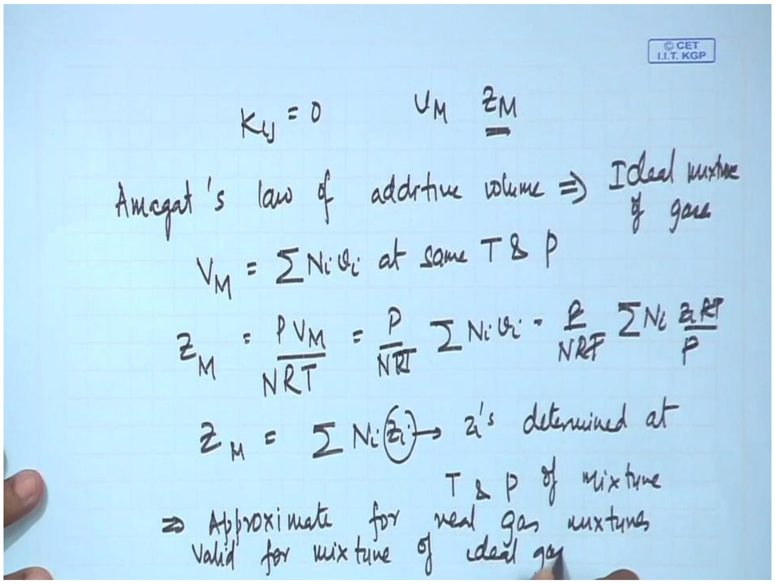

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$z_M = \sum N_i \boxed{z_i} \rightarrow$ $z_i$'s determined at T & P of mixture

⇒ Approximate for real gas mixtures

Valid for mixture of ideal gas

Well, so to continue with our discussions we had left the discussion in the last class when you're trying to find out zM in terms of Amagat's law of additive volume and as I had said in terms of Daltons law of additive pressure. Now we have already derived from the Amagat's law of additive volume, what did we give? We expressed zM in terms of zi where all the zi's has been determined at the T and P of the mixture, fine. So therefore this as I have said, this is approximate for real gas mixtures and valid for mixture of ideal gases, right?

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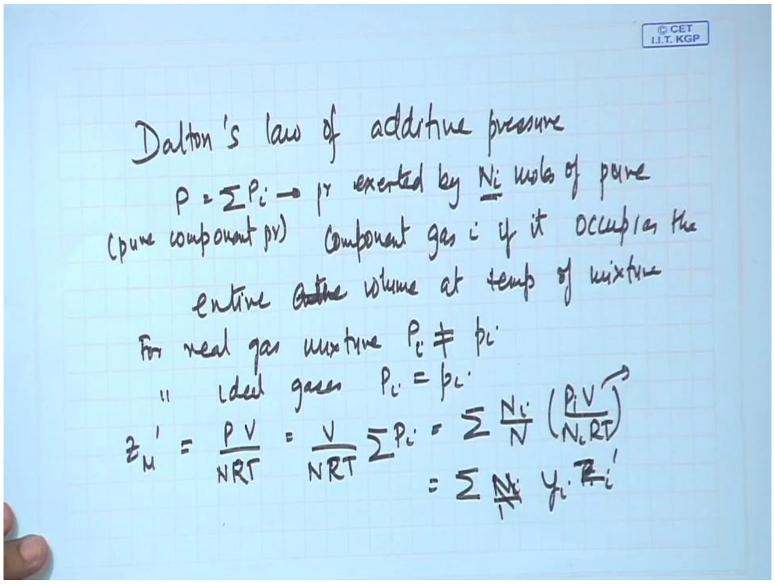

Dalton's law of additive pressure

$P = \sum P_i \rightarrow$ pr exerted by $\underline{N_i}$ moles of pure component gas i if it occupies the entire ~~entire~~ volume at temp of mixture

(pure component pr)

For real gas mixture $P_i \neq p_i$

" ideal gases $P_i = p_i$

$$z_M' = \frac{PV}{NRT} = \frac{V}{NRT}\sum P_i = \sum \frac{N_i}{N}\left(\frac{P_i V}{N_i RT}\right)$$
$$= \sum \cancel{N_i}\, y_i \cdot \cancel{z}_i'$$

Now let us take up the other law for finding out the partial pressure all of us know this is nothing but Daltons law of additive pressure, what does it say? It tells us that total pressure exerted by an ideal gas mixture it is nothing but the sum of the partial pressure or in other words the pressure of the gas mixture it is nothing but the pure component pressure.

What is this? This is the pure component pressure which is pressure exerted by Ni moles of pure component gas i if it occupies the entire volume V at temperature of the mixture. So therefore T mixture and T pure components are the same and the partial pressure it's nothing it is simply the pressure exerted by Ni moles of the gas if it occupied the entire volume.

Now just it's important to remember that for real gas mixtures it can happen that the pure component pressure the Pi this is usually known as the pure component pressure, okay. This pure component pressure may not be equal to the partial pressure, it can happen if interactions are quite dissimilar but for ideal gases we always have Pi equals to pi, fine.

Now in this case letters found find out zM prime I have just written the prime just to differentiate the mixture compressibility factor obtained from Amagat's law and the mixture compressibility factor obtained from Dalton's law.

Now what is zM prime equals to, this is nothing but equals to P the total pressure V by NRT which can be written down as V by NRT Sigma of Pi which is nothing but equal to Sigma of Ni by N PiV by NiRT, fine. Now what is this? This is also a form of z, so therefore can I not write it down as Ni by or else I write it down as yi considering that this is a gaseous mixture into Zi prime. So therefore from both the equations what have you got?

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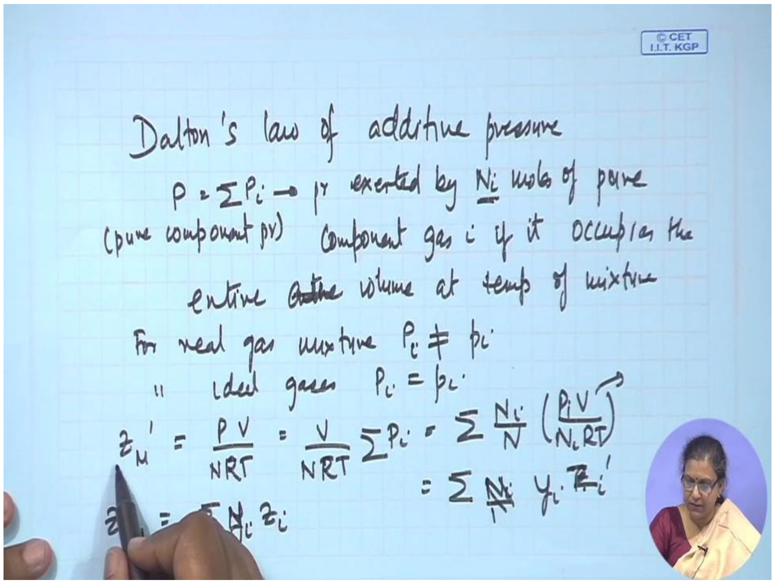

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$$z_M = \sum y_i z_i$$

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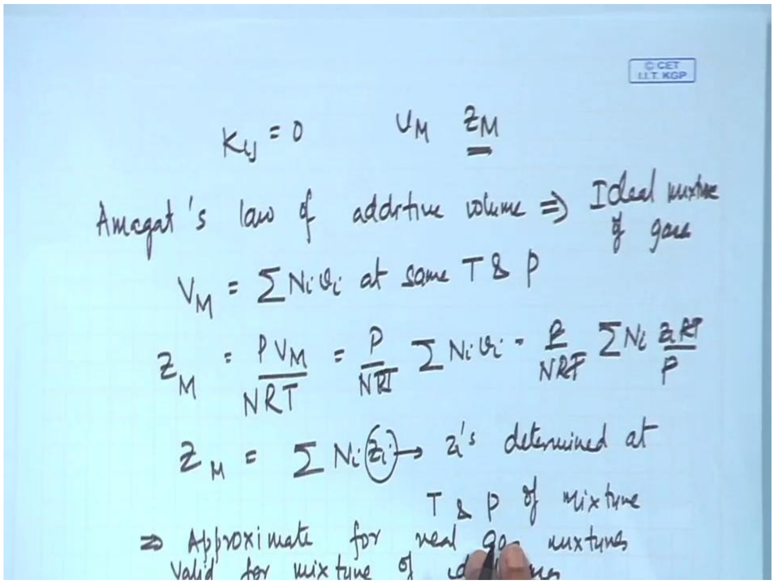

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$$z_M = \sum N_i \xrightarrow{} \bigcirc\!\!\!\!\!z_i$$

$z_i$'s determined at T & P of mixture

$\Rightarrow$ Approximate for real ga mixtures

Valid for mixture of

If I just write down the other equation here just for comparison we get zM is equals to, sorry this is yi zi, fine. Now just see the difference between the 2, I can predict the mixture compressibility factor either by using the Amagat’s law of additive volumes which I have derived here or the Dalton’s law of partial pressure.

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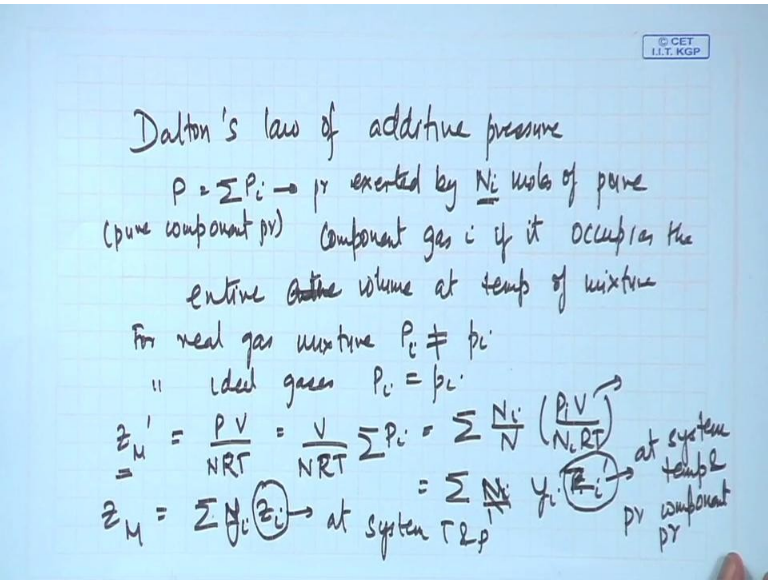

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$$\underline{Z_M'} = \frac{PV}{NRT} = \frac{V}{NRT} \sum P_i = \sum \frac{N_i}{N} \left( \frac{P_i V}{N_i RT} \right)$$

$$= \sum \cancel{N_i}\, y_i \boxed{Z_i'} \rightarrow \text{at system temp \& pr component pr}$$

$$Z_M = \sum y_i \boxed{Z_i} \rightarrow \text{at system T \& p}$$

We find that from Dalton's law of partial pressure the mixture compressibility factor is defined in terms of the pure component compressibility factor where this is taken at system temperature and pure component pressure this is something very important. So in this case we express it in system temperature and pure component pressure or the pressure which this particular gas would have exerted had it occupied the entire volume.

While from Amagat's law we express it in terms of the pure component compressibility factors where these are expressed at system temperature and pressure.

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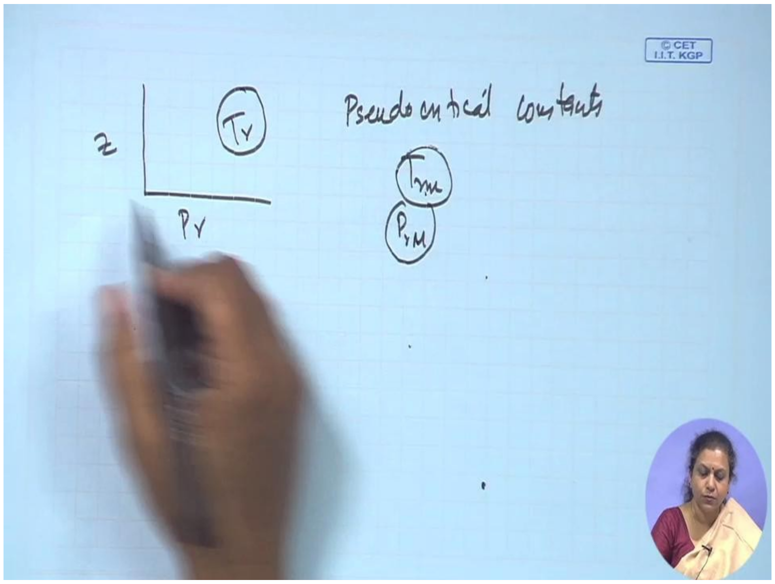

So well, this was one the other way of finding out Z is we had already discussed apart from the cubic equations and the virial equations of state, we had also discussed the compressibility factor charts where we have shown z is a function of Pr and Tr, right? So therefore from these equations suppose there is some particular way of finding out the pseudo critical constants as it is said.

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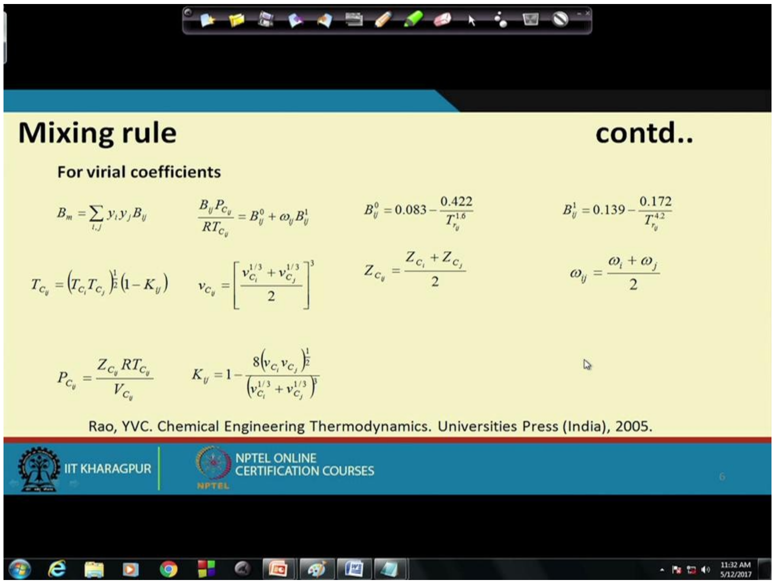

## Mixing rule contd..

For virial coefficients

$$B_m = \sum_{i,j} y_i y_j B_{ij} \qquad \frac{B_{ij} P_{C_{ij}}}{R T_{C_{ij}}} = B_{ij}^0 + \omega_{ij} B_{ij}^1 \qquad B_{ij}^0 = 0.083 - \frac{0.422}{T_{r_{ij}}^{1.6}} \qquad B_{ij}^1 = 0.139 - \frac{0.172}{T_{r_{ij}}^{4.2}}$$

$$T_{C_{ij}} = \left(T_{C_i} T_{C_j}\right)^{\frac{1}{2}} \left(1 - K_{ij}\right) \qquad v_{C_{ij}} = \left[\frac{v_{C_i}^{1/3} + v_{C_j}^{1/3}}{2}\right]^3 \qquad Z_{C_{ij}} = \frac{Z_{C_i} + Z_{C_j}}{2} \qquad \omega_{ij} = \frac{\omega_i + \omega_j}{2}$$

$$P_{C_{ij}} = \frac{Z_{C_{ij}} R T_{C_{ij}}}{V_{C_{ij}}} \qquad K_{ij} = 1 - \frac{8\left(v_{C_i} v_{C_j}\right)^{\frac{1}{2}}}{\left(v_{C_i}^{1/3} + v_{C_j}^{1/3}\right)^3}$$

Rao, YVC. Chemical Engineering Thermodynamics. Universities Press (India), 2005.

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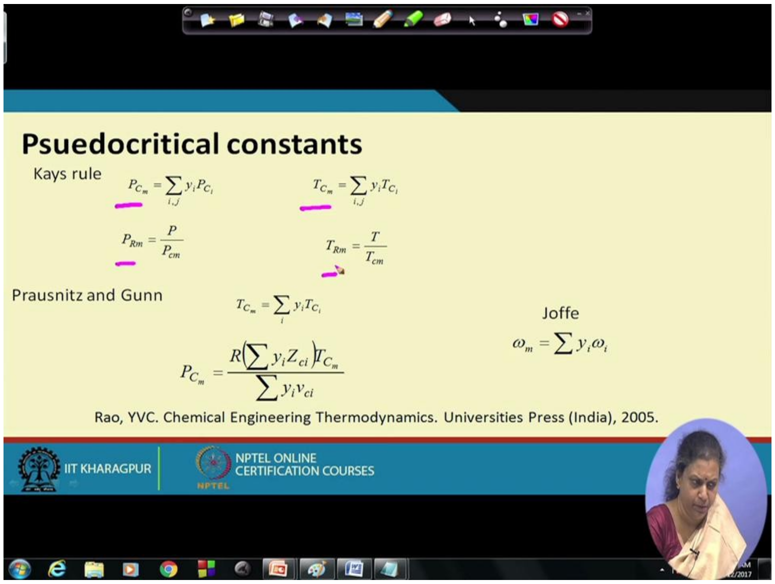

## Psuedocritical constants

Kays rule

$$P_{C_m} = \sum_{i,j} y_i P_{C_i} \qquad T_{C_m} = \sum_{i,j} y_i T_{C_i}$$

$$P_{Rm} = \frac{P}{P_{cm}} \qquad T_{Rm} = \frac{T}{T_{cm}}$$

Prausnitz and Gunn

$$T_{C_m} = \sum_i y_i T_{C_i}$$

$$P_{C_m} = \frac{R\left(\sum y_i Z_{ci}\right) T_{C_m}}{\sum y_i v_{ci}}$$

Joffe

$$\omega_m = \sum y_i \omega_i$$

Rao, YVC. Chemical Engineering Thermodynamics. Universities Press (India), 2005.

Suppose we can find out the Trm and Prm for the mixture case then using these 2 values, since we know that the compressibility factor chart it is applicable for all particular substances so therefore what we can do? We can find out if we can propose some pseudo-critical constants then in that case using the compressibility factor chart also we should be in a position to find out Z.

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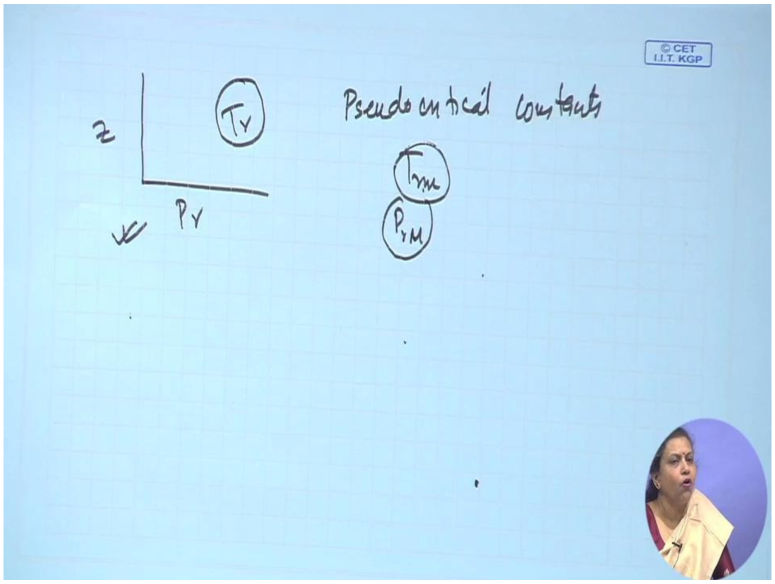

Now usually there are several again mixing rules for finding out the pseudo critical constants, we find that there is a Kays rule which gives the mixture the Pcm the critical pressure of the mixture and the Tcm, both as additive function of pure component critical constants from where the reduced components can be found out and this particular graph can be used but usually we find out that although in from the Tcm value gives quite accurate cases. Again in this particular case since the mixture critical pressure again is a function of the interaction of the different molecules in the mixture.

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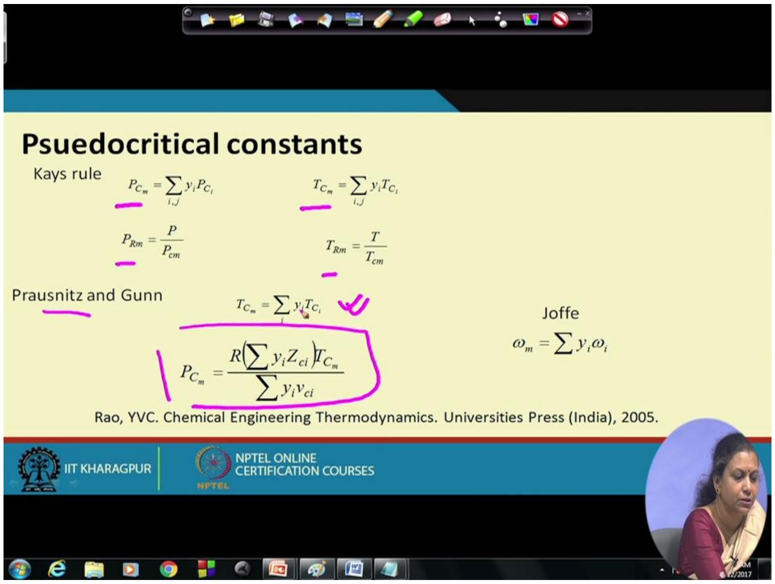

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So naturally the additive equation does not usually does not hold good and accordingly another equation has been proposed by Prausnitz and Gunn, this particular equation along with the additive law for the mixture critical temperature these 2 combined they give a better result and so therefore usually what is recommended is you use this particular Tcm you use this particular Pcm and then you try to use this particular compressibility factor chart for better results.

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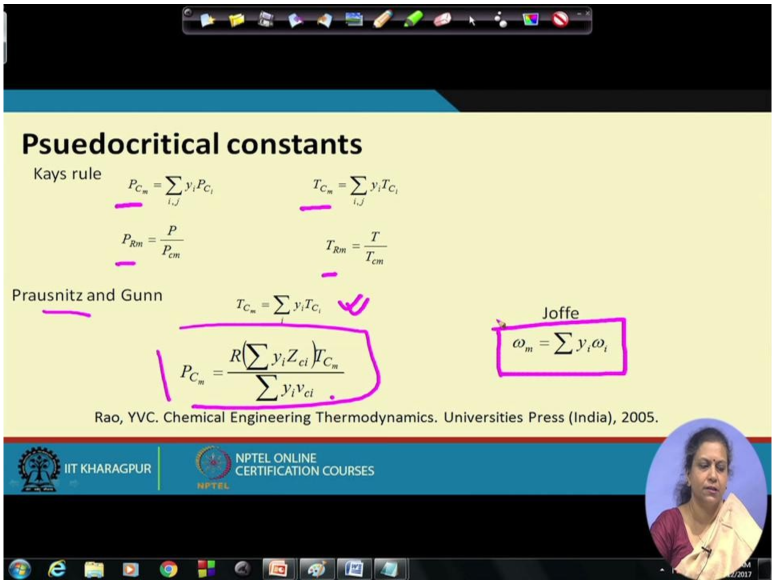

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And if you’re going for a 3 parameter law of corresponding states then usually this particular equation is used to find out the mixture acentric factor in terms of the component acentric factors. Now so with this, what I do? I have finished up or rather I have covered the estimation of properties of real gas mixtures or for that matter estimation of total properties of any particular mixture in terms of the properties of the pure components.

And I have proposed different mixing rules and I have proposed different combining rules, so now suppose I would like to predict the fugacity of the component, right?

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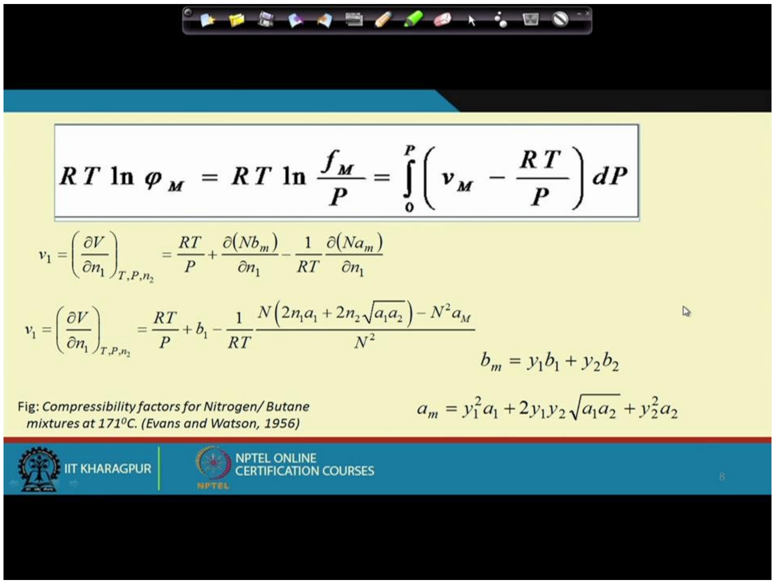

$$RT \ln \varphi_M = RT \ln \frac{f_M}{P} = \int_0^P \left( v_M - \frac{RT}{P} \right) dP$$

$$v_1 = \left( \frac{\partial V}{\partial n_1} \right)_{T,P,n_2} = \frac{RT}{P} + \frac{\partial (N b_m)}{\partial n_1} - \frac{1}{RT} \frac{\partial (N a_m)}{\partial n_1}$$

$$v_1 = \left( \frac{\partial V}{\partial n_1} \right)_{T,P,n_2} = \frac{RT}{P} + b_1 - \frac{1}{RT} \frac{N\left(2n_1 a_1 + 2n_2 \sqrt{a_1 a_2}\right) - N^2 a_M}{N^2}$$

$$b_m = y_1 b_1 + y_2 b_2$$

Fig: *Compressibility factors for Nitrogen/ Butane mixtures at 171⁰C. (Evans and Watson, 1956)*

$$a_m = y_1^2 a_1 + 2 y_1 y_2 \sqrt{a_1 a_2} + y_2^2 a_2$$

So for predicting the fugacity of the mixture this is the equation, right? So therefore for other things it is pretty straightforward if you want to predict h, s, u, a, g you can do it. Let us take up the fugacity of the mixture. Simply for finding out the fugacity of the mixture what we need? We need to know the molar volume of the mixture, right?

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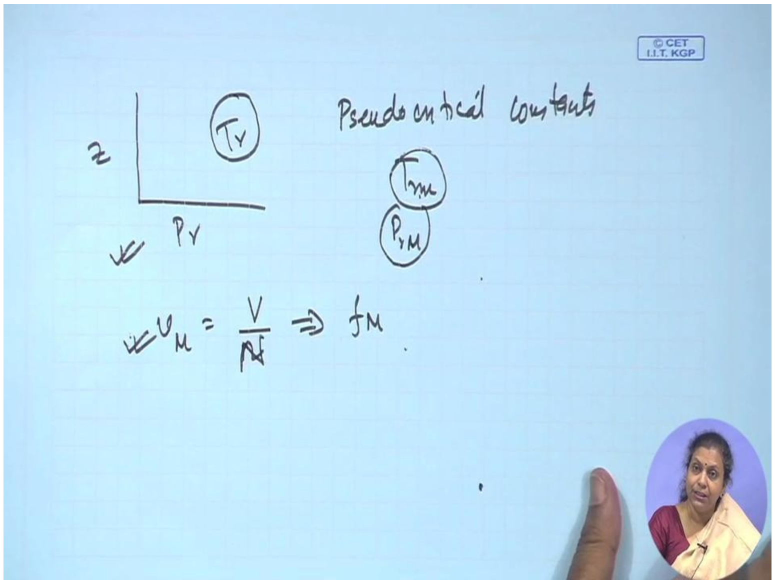

What is the molar volume of the mixture? This vM this is nothing but equal to the total volume divided by capital N the total number of moles of the mixture, it is not very difficult to find out this equation and from here we can find out the value of fM, right? But we need to remember what is the purpose of the fugacity?

Why did we define fugacity? Fugacity was defined in order to provide a quantitative prediction of phase equilibrium in terms of some physically realizable quantity, right? So therefore we had if you recollect in the while we're discussing fugacity what we would do? We reframe the entire condition of equilibrium in terms of temperature, pressure and fugacity. What was the condition for fugacity which refers to chemical equilibrium if you remember?

It was fi alpha equals to fi beta which says that the fugacity of each component i in the different phases should be equal. So therefore if we really want to find out whether 2 phases are in equilibrium what do we need to calculate? We do not need to calculate fM, on the contrary we need to calculate the fugacity of the individual components in the different phases, right?

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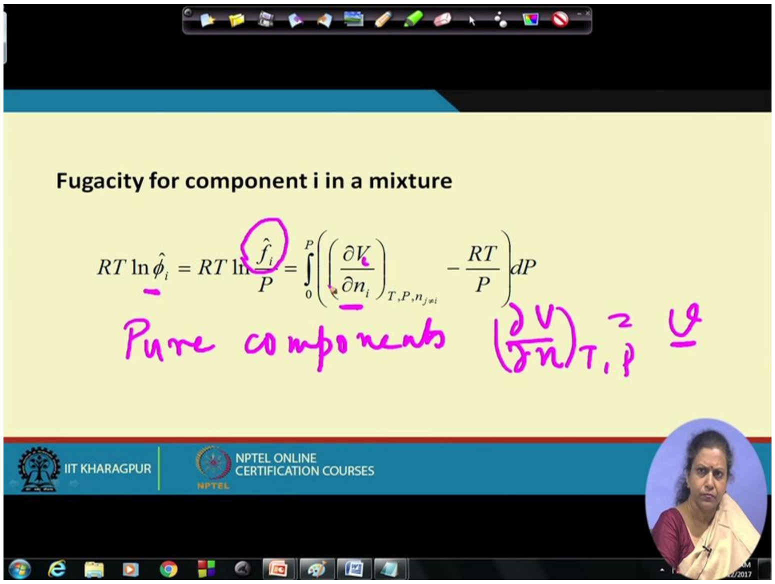

**Fugacity for component i in a mixture**

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

Pure components $\left(\frac{\partial V}{\partial n}\right)_{T,P} \overset{?}{=} v$

So rather than this particular equation what we would need under that condition is the equation which I have written down here. So if I have to write down this equation what do we find? Just for the time being you just note that this refers to fugacity coefficient of component i in the mixture, this refers to the fugacity of component i in the mixture, right?

We will have more discussions because this is something very special and very different from other molar properties of components in mixtures. So therefore for this, what do we need? We need to find how the volume of this particular component the total volume Vi of the component varies with ni? This particular data we need.

Now what is this data? For pure components we know suppose we are dealing with pure components, so therefore under that condition this particular del V del n at constant TP it is nothing but the molar volume very easy to find out but in this particular case, can we simply substitute the molar volume in this particular equation?

Or will the volume contributed, the contribution of the volume of component i when it is in a mixture be different as compared to the contribution of component i when it is added to its own particular system. What I mean to say, that when i is added in a large amount of i, suppose one mole of i is added to a large volume of i, it contributes its molar volume to the mixture, the mixture volume increases by the molar volume of component i.

Now if the same component i, I mix it or I add to a large volume of say component J then in this particular case is it going to contribute its molar volume or is it going to going to contribute something different from the molar volume? So therefore we discuss all this things regarding the partial molar properties as they’re called in the next class and then it will be easy for us to understand how we have we can predict the fugacities of components in mixtures and then from them that how we can find out the phase or rather how we can deal with different phase equilibrium problems?