Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
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Lecture 30
Mixtures

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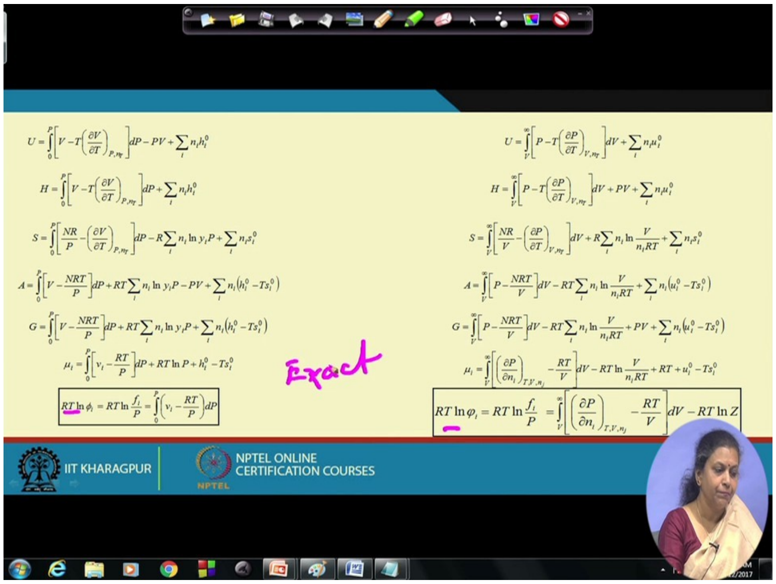

$$U=\int_0^P\left[V-T\left(\frac{\partial V}{\partial T}\right)_{P,n_T}\right]dP-PV+\sum_i n_i h_i^0$$

$$H=\int_0^P\left[V-T\left(\frac{\partial V}{\partial T}\right)_{P,n_T}\right]dP+\sum_i n_i h_i^0$$

$$S=\int_0^P\left[\frac{NR}{P}-\left(\frac{\partial V}{\partial T}\right)_{P,n_T}\right]dP-R\sum_i n_i \ln y_i P+\sum_i n_i s_i^0$$

$$A=\int_0^P\left[V-\frac{NRT}{P}\right]dP+RT\sum_i n_i \ln y_i P-PV+\sum_i n_i\left(h_i^0-Ts_i^0\right)$$

$$G=\int_0^P\left[V-\frac{NRT}{P}\right]dP+RT\sum_i n_i \ln y_i P+\sum_i n_i\left(h_i^0-Ts_i^0\right)$$

$$\mu_i=\int_0^P\left[v_i-\frac{RT}{P}\right]dP+RT\ln P+h_i^0-Ts_i^0$$

$$\boxed{\underline{RT\ln}\,\phi_i=RT\ln\frac{f_i}{P}=\int_0^P\left(v_i-\frac{RT}{P}\right)dP}$$

Exact

$$U=\int_V^\infty\left[P-T\left(\frac{\partial P}{\partial T}\right)_{V,n_T}\right]dV+\sum_i n_i u_i^0$$

$$H=\int_V^\infty\left[P-T\left(\frac{\partial P}{\partial T}\right)_{V,n_T}\right]dV+PV+\sum_i n_i u_i^0$$

$$S=\int_V^\infty\left[\frac{NR}{V}-\left(\frac{\partial P}{\partial T}\right)_{V,n_T}\right]dV+R\sum_i n_i \ln\frac{V}{n_i RT}+\sum_i n_i s_i^0$$

$$A=\int_V^\infty\left[P-\frac{NRT}{V}\right]dV-RT\sum_i n_i \ln\frac{V}{n_i RT}+\sum_i n_i\left(u_i^0-Ts_i^0\right)$$

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$$\mu_i=\int_V^\infty\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}-\frac{RT}{V}\right]dV-RT\ln\frac{V}{n_i RT}+RT+u_i^0-Ts_i^0$$

$$\boxed{\underline{RT}\ln\varphi_i=RT\ln\frac{f_i}{P}=\int_V^\infty\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}-\frac{RT}{V}\right]dV-RT\ln Z}$$

Well, hello everybody so till the last class what were we discussing, we were trying to discuss different sort of characteristics the properties of pure components or single component or single component solution and till date whatever we have done, we have come across a post of equations which I have just I have just listed the summary of it in this particular slide. Now you will be recalling that several times we have seen that the properties they demand data of say volume as a function of pressure.

While on the other hand we find that most of the equations which we have dealt till now say the cubic equations of state primarily they express pressure in terms of volume and temperature. So what I have done in this particular slide? I have noted down all the equations both in pressure explicit form as well as in volume explicit form. From this particular chart what do we see? We find that for any particular substance regarding of whether it is pure or it is a mixture all the thermodynamic properties of interest in phase equilibrium can be calculated from thermal data and volumetric data.

We take up any particular equation we find that in both the equations they comprise of thermal data which suggests how the properties concerned properties varies with temperature under conditions of constant pressure or constant density and we also need volumetric data which gives us how the particular thermodynamic function it varies with pressure or density at constant temperature. Now we would also like to remember that all these equations which have been given they are for single component substances when there is no phase change.

When we have additional phase change then we require additional volumetric as well as thermal data to account for the phase change situation we also see that very frequently we would like to express the property change in terms of the property which the substance would have in the ideal gas state under the conditions of same temperature same pressure, a typical example of this is the fugacity of the component.

If you observe the equations of fugacity in this particular equation and in this particular equation, we find that in both the equations they have expressed fugacity in terms of the corresponding value under the ideal gas state keeping in mind that the fugacity for an ideal gas is its pressure under that condition of temperature or its partial pressure under the condition of constant temperature and composition.

Now if you go through all these equations what do we find? We find that for all these equations the only data that we require, see solving these equations are not at all a problem they are just simple integration techniques. And I would also like to remind you 2 things usually we are tempted to think that all these equations are applicable for gases, it is not so these equations again I repeat they are applicable for any substance in pure state, mixed state whether it is a component in a mixture whether it is ideal whether it is non-ideal whether it is a gas whether it is a condensed phase for all particular situations the equations are applicable number 1.

The equations have been written for pure components only number 2 and the most important thing which I would like to suggest or to bring to your attention is that all the equations which I have mentioned here all the equations they are exact equations, whatever equations we have mentioned they have no simplifying assumptions they are exact equations and they are not restricted to the vapor phase only. Now for solving these equations what is the only thing that we require?

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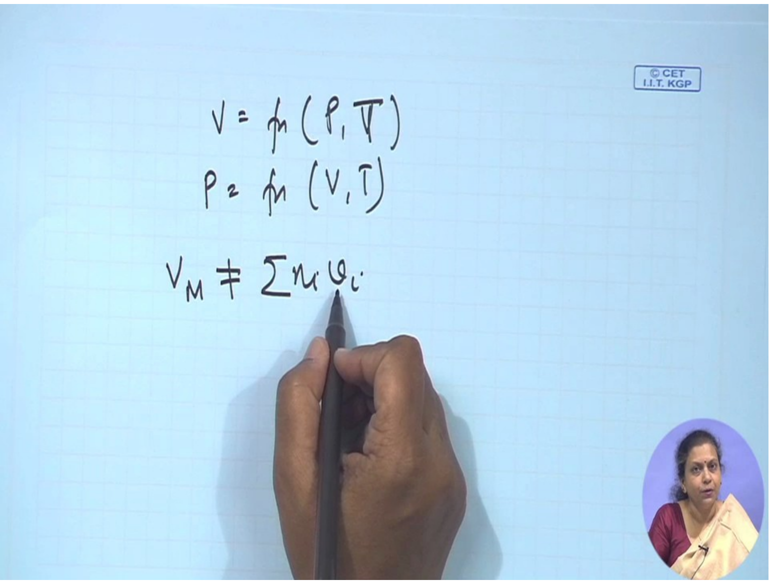

$$V = fn(P, T)$$
$$P = fn(V, T)$$
$$V_M \neq \sum n_i v_i$$

For solving the equations we just need say either volume as a function of P, V sorry P, T or maybe we require pressure as a function of V, T. Normally we have also discussed in the PvT behavior of gases several types of equations for example we have discussed the cubic equations, the compressibility factor chart, the virial equations of state when we should use what everything is fine but I would also like to remind you that they need for such a large number of equations was because no particular equation is applicable over a large range of temperature, pressure and composition conditions.

The situation becomes much graver when we start dealing with mixtures and we all know that mixtures are the things that we actually deal in practical situations there are very few pure components situations that we deal. So therefore if we have to deal with mixtures if I really want to find out the property changes in case of mixtures from these particular equations what do I need? I need to replace all these, these are total volume of the mixtures, so then I have to express total volume of the mixtures in terms of the molar volume of the mixture and what do I need for that?

I need some particular way to estimate the total volume from the molar volume and here I would just like to mention that it is not always the case that I know the molar volume of pure component mixtures and I can just write that the total volume of the mixture is often not equal to the equal to the number of moles times the molar volume of the pure components we will be coming to it shortly but before that I would like to mention that if we are supposed to use these particular equations for finding out mixture properties the only obstruction or the only hitch which we face are not these equations.

These equations they are exact they give very accurate results, we can use them for any purpose, the only problem is in order to solve these equations we need something of this sort and when we are doing it for a mixture then we have additional variables which are the compositions or the mole numbers of the different constitutions in the mixture.

So therefore finding such a particular equation of state which will be valid and it is not that we have to find one particular equation of state at some particular conditions of temperature and pressure, just go through all the equations for every equation there is an integral sign because as I have told you we cannot predict the absolute value of properties.

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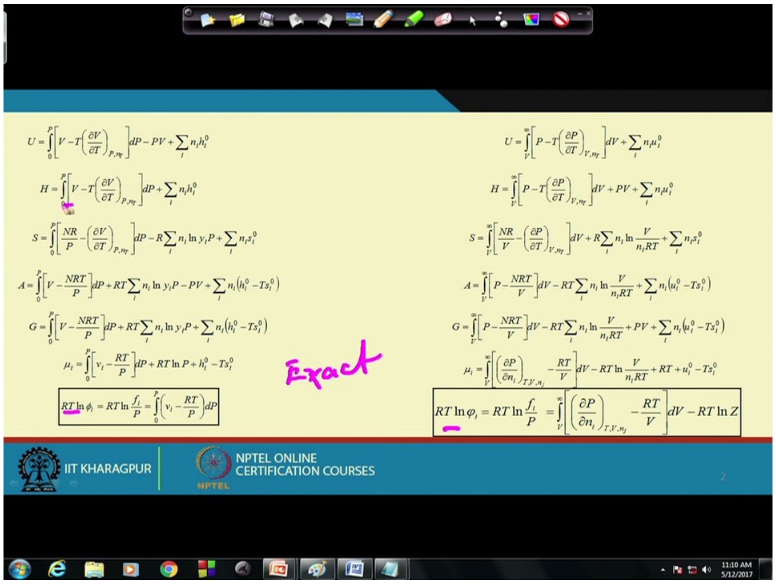

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$$A = \int_0^P \left[V - \frac{NRT}{P}\right]dP + RT\sum_i n_i \ln y_i P - PV + \sum_i n_i\left(h_i^0 - Ts_i^0\right)$$

$$G = \int_0^P \left[V - \frac{NRT}{P}\right]dP + RT\sum_i n_i \ln y_i P + \sum_i n_i\left(h_i^0 - Ts_i^0\right)$$

$$\mu_i = \int_0^P \left[v_i - \frac{RT}{P}\right]dP + RT\ln P + h_i^0 - Ts_i^0$$

$$\boxed{RT\ln\phi_i = RT\ln\frac{f_i}{P} = \int_0^P \left(v_i - \frac{RT}{P}\right)dP}$$

Exact

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$$\mu_i = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right]dV - RT\ln\frac{V}{n_i RT} + RT + u_i^0 - Ts_i^0$$

$$\boxed{RT\ln\varphi_i = RT\ln\frac{f_i}{P} = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right]dV - RT\ln Z}$$

So therefore we have to integrate it from one particular lower limit to the other upper limit and during this entire limit I need to know this particular expression I need to know how V varies with T not only at P the pressure of interest but from P equals to 0 to P equals to P. Now this is a very difficult situation we have large number of equations of states but finding a unique equation of state which is going to be applicable from almost very low pressure to the pressure of interest for the different components which are present in a particular mixture is very difficult.

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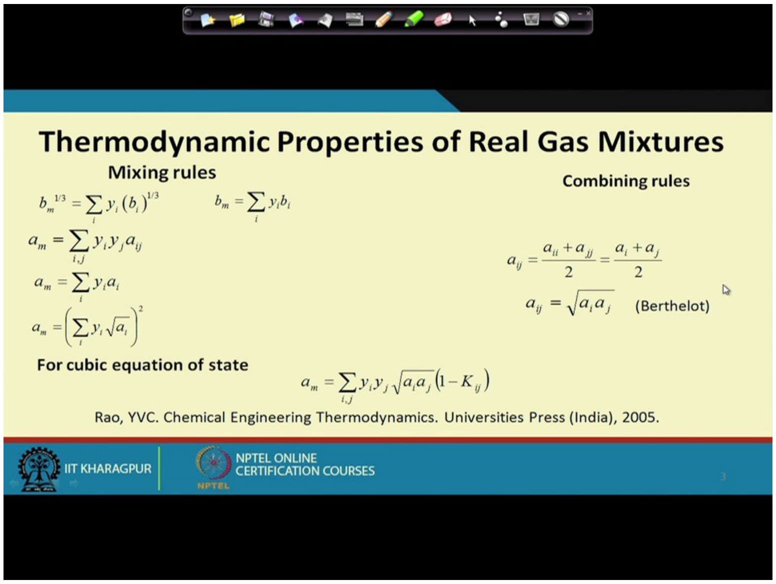

Thermodynamic Properties of Real Gas Mixtures

Mixing rules

$$b_m^{1/3} = \sum_i y_i (b_i)^{1/3} \qquad b_m = \sum_i y_i b_i$$

$$a_m = \sum_{i,j} y_i y_j a_{ij}$$

$$a_m = \sum_i y_i a_i$$

$$a_m = \left(\sum_i y_i \sqrt{a_i}\right)^2$$

Combining rules

$$a_{ij} = \frac{a_{ii} + a_{jj}}{2} = \frac{a_i + a_j}{2}$$

$$a_{ij} = \sqrt{a_i a_j} \quad \text{(Berthelot)}$$

For cubic equation of state

$$a_m = \sum_{i,j} y_i y_j \sqrt{a_i a_j}\,(1 - K_{ij})$$

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

So therefore today we are going to discuss the different mixing rules and combining rules which we use in order to evaluate mixture properties in terms of pure component properties. Now in this particular respect I would like to mention that in reality if we have to mention, if we really have to find out the mixture properties from the pure component properties we need to have a proper idea of the molecule considerations the exact equations are going to come from molecular considerations.

But unfortunately at the present moment we do not have that much idea about the behavior at the molecular level the interactions of the different components at the molecule level. So therefore most of the cases the rules which we suggest for finding out the mixture constants in terms of the individual property constants they are empirical in nature since they have been found to work well for a large number of conditions we just adopt them.

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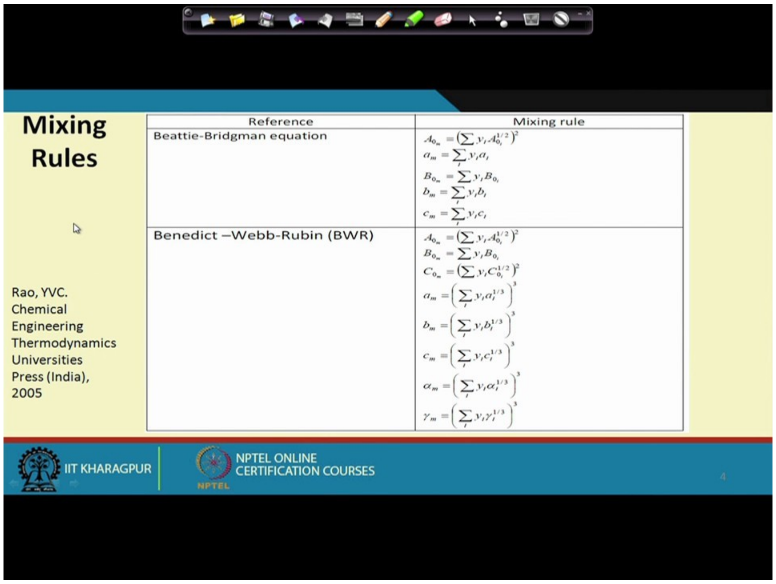

Mixing Rules

Reference	Mixing rule
Beattie-Bridgman equation	$A_{0_m} = (\sum y_i A_{0_i}^{1/2})^2$ $a_m = \sum_i y_i a_i$ $B_{0_m} = \sum y_i B_{0_i}$ $b_m = \sum_i y_i b_i$ $c_m = \sum_i y_i c_i$
Benedict –Webb-Rubin (BWR)	$A_{0_m} = (\sum y_i A_{0_i}^{1/2})^2$ $B_{0_m} = \sum y_i B_{0_i}$ $C_{0_m} = (\sum y_i C_{0_i}^{1/2})^2$ $a_m = \left(\sum_i y_i a_i^{1/3}\right)^3$ $b_m = \left(\sum_i y_i b_i^{1/3}\right)^3$ $c_m = \left(\sum_i y_i c_i^{1/3}\right)^3$ $\alpha_m = \left(\sum_i y_i \alpha_i^{1/3}\right)^3$ $\gamma_m = \left(\sum_i y_i \gamma_i^{1/3}\right)^3$

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

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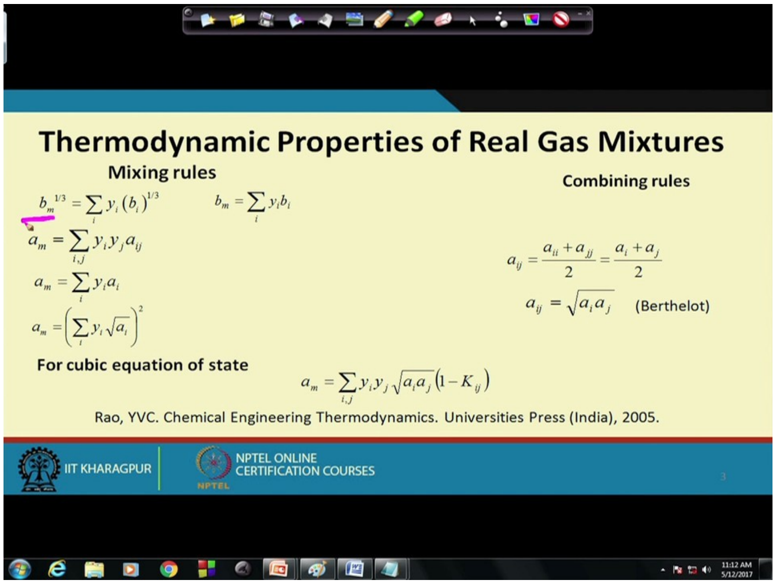

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$$a_{ij} = \sqrt{a_i a_j} \quad \text{(Berthelot)}$$

For cubic equation of state

$$a_m = \sum_{i,j} y_i y_j \sqrt{a_i a_j}\,(1 - K_{ij})$$

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Now here I have just noted down a few mixture properties which or rather a few mixing rules for which can be used or which can be used to predict the constants of the equations in terms of pure component constants. Now here I would like to mention that suppose we take up any particular say suppose for example we take up the Van der waals equations of state.

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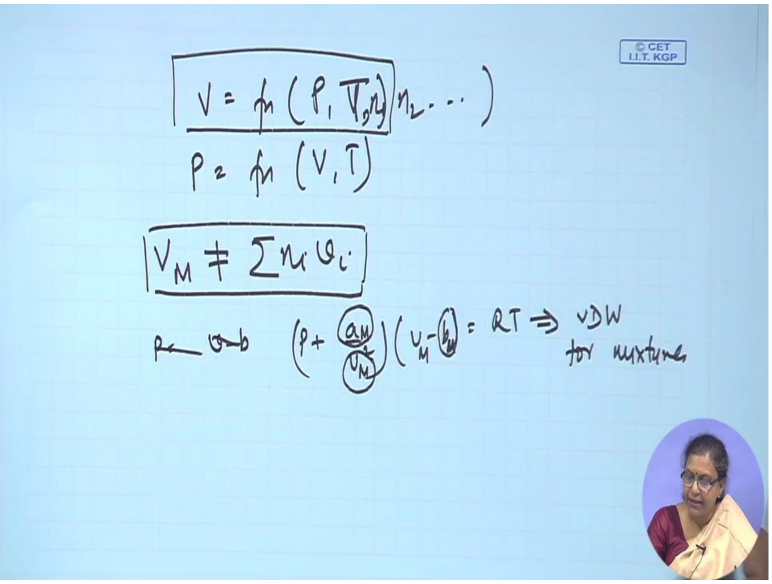

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$$\boxed{V = fn(P, T, n_1, n_2 \ldots)}$$

$$P = fn(V, T)$$

$$\boxed{V_M \neq \sum n_i v_i}$$

$$P \leftarrow v - b \qquad \left(P + \frac{a_M}{v_M^2}\right)(v_M - b_M) = RT \Rightarrow \text{VDW for mixtures}$$

Now for Van der waals equation of state we find that the first thing which we need if we have to use the Van der waals equation of state say v minus b or else I will write it in the proper form P plus a by v square into v minus b equals to RT, for gaseous mixture this becomes M, this becomes M, this becomes M, this becomes M, this becomes M. So I need something to find out aM, I need to find out vM and I need to find out bM and once these can be accurately predicted then this particular Van der waals equation can be used for mixtures under the conditions where it is applicable.

You already know that we cannot use this equation for P greater than 200 atmospheres this is not very accurate for the close to the liquid vapor coexistence conditions but other than that for normal conditions we can use it provided we can find out this particular constants. Now usually there are different ways or different rules have been proposed, keep in mind that so many rules have been proposed just because none of them work very well, all of them are empirical in nature.

So for example if you take up b from where does b come, if you recollect b is nothing but it is the correction due to the volume occupied by the molecules in ideal gas state we assume negligible volume of the molecules as compared to the volume of the entire gas. So therefore bM it should be somehow related to the size of the molecules.

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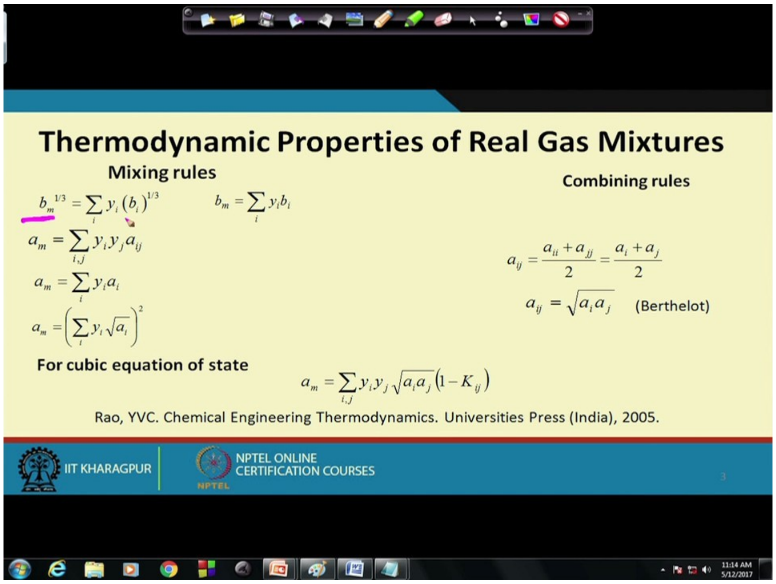

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$$a_{ij} = \sqrt{a_i a_j} \quad \text{(Berthelot)}$$

For cubic equation of state

$$a_m = \sum_{i,j} y_i y_j \sqrt{a_i a_j} \left(1 - K_{ij}\right)$$

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

Now there are 2 ways of expressing bM as I have written down in this particular slide the first one, what does it assume? It assumes that we have spherical molecules and it assumes additivity of diameter, right? From assuming additivity of diameter the bM is given in the form that I have have written down here but usually the more popular thing which the people usually use is they assume additivity of volumes other than diameters.

Under that case we find that the mixture b is simply an additive property of the pure component b and this is quite a popular equation and this is usually normally used but remember one thing choosing a correct mixing rule again I should mention it is not possible because all mixing rules they are based on different assumptions to which assumptions are going to hold under different conditions is not very clear.

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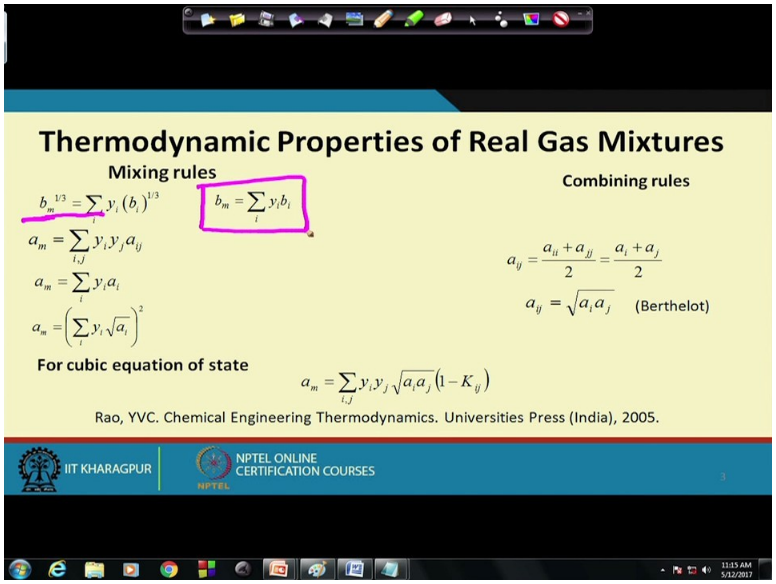

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Any way b it’s not very difficult you can use either but for most of the cases we use this particular equation and for this class we will be using this particular equation.

Now let us come to the a if you recall a was introduced just to take into account the interaction between the different molecules so therefore at moderate densities for mixtures whose molecules are not very dis-similar in size we find that the mixing rules for b does not significantly affect the prediction of the results but the influence of a on the results are much more important.

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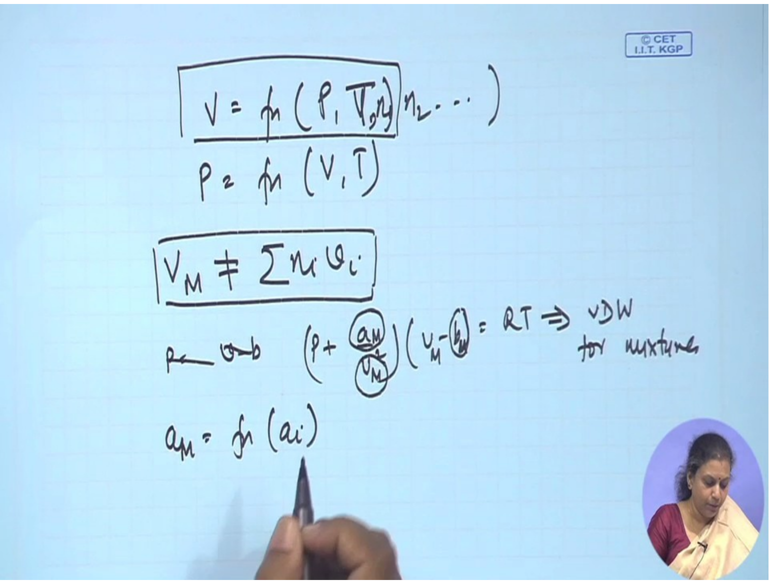

$$\boxed{V = fn(P, T, n_1, n_2 \ldots)}$$

$$P = fn(V, T)$$

$$\boxed{V_M \neq \sum n_i v_i}$$

~~P~~ ~~v-b~~ $\left(P + \frac{a_M}{v_M^2}\right)(v_M - b_M) = RT \Rightarrow$ VDW for mixture

$$a_M = fn(a_i)$$

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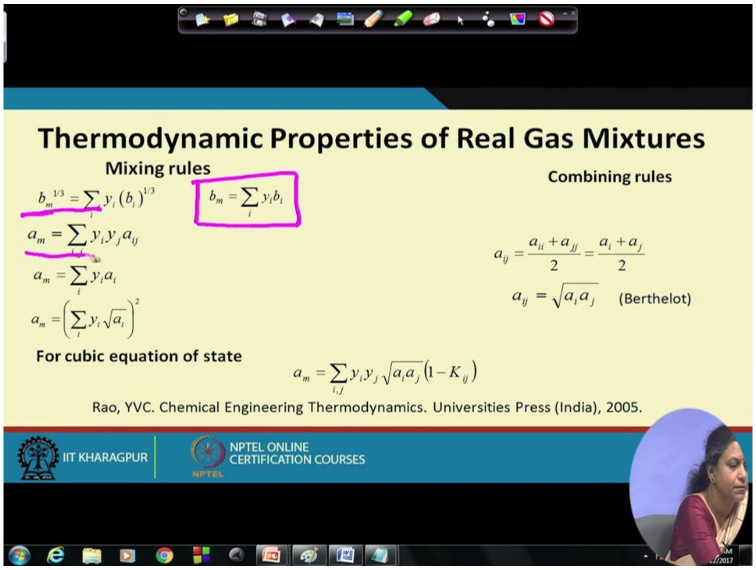

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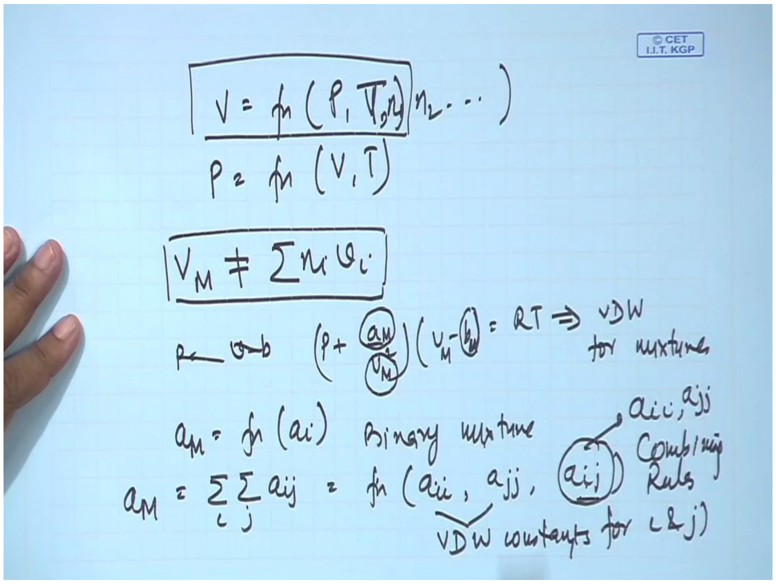

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$$P = fn(V, T)$$

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$$P \leftarrow \quad v \rightarrow b \qquad \left(P + \frac{a_M}{V_M^2}\right)(V_M - b_M) = RT \Rightarrow \text{VDW for mixtures}$$

$$a_M = fn(a_i) \qquad \text{Binary mixture}$$

$$a_M = \sum_i \sum_j a_{ij} = fn(\underbrace{a_{ii}, a_{jj}}_{\text{VDW constants for } i \,\&\, j}, a_{ij}) \qquad a_{ii}; a_{jj} \quad \text{Combining Rules}$$

So it is very important to or rather to propose a proper relationship for finding out aM in terms of the component a's. Now in this particular aspect usually what is the most popular rule which is used is written down here, this says that aM it is a summation of in fact it is a double integral i and j suppose there are 2 molecules it is for a binary mixture it is a summation of aij where i and j can be same i and j can be different.

So therefore for a just for a binary mixture for what do we get from here? For a binary mixture it should comprise it should be a function of aii the interactions between the molecules of component i it should be a function of ajj which is again arises due to the interaction between the molecules of j, now these 2 they can be obtained from the Van der waals constants for component i and component j but apart from that we would also have something like aij.

What is this aij? This takes into account the interaction between molecule i and molecule j. Now aij can be equated to aii or ajj provided the molecules they are all similar in nature which is usually not the case in under those circumstances when usually this case is when i and j they are the similar molecules then there should be some way of predicting again aij in terms of aii and ajj.

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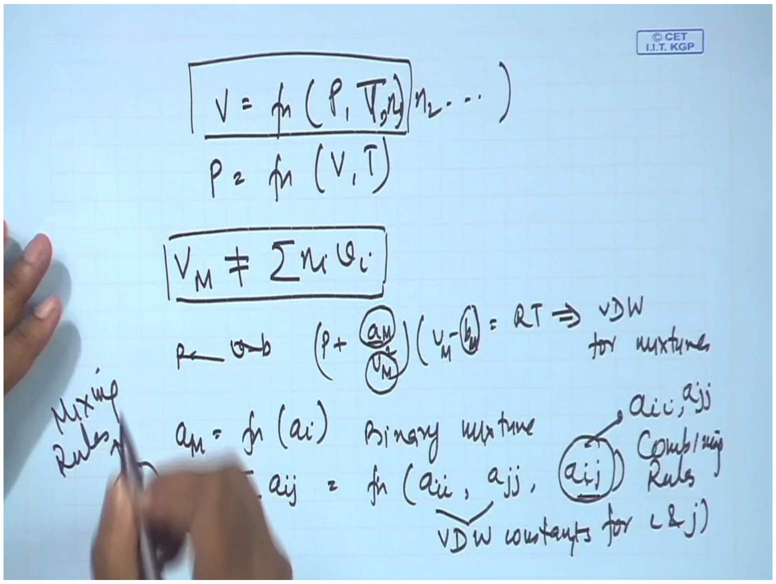

Now the rules which suggest how to predict the interaction parameters in terms of the mixing parameters those rules are known as the combining rules and the rules which predict the mixture constants in terms of pure component constants they are known as the mixing rules.

So therefore I repeat once more the mixing rules are the equations which express mixture constants in terms of pure component constants and combining rules are the equations which provide the interaction terms when the different components are there in terms of the interaction parameters of the pure component constants.

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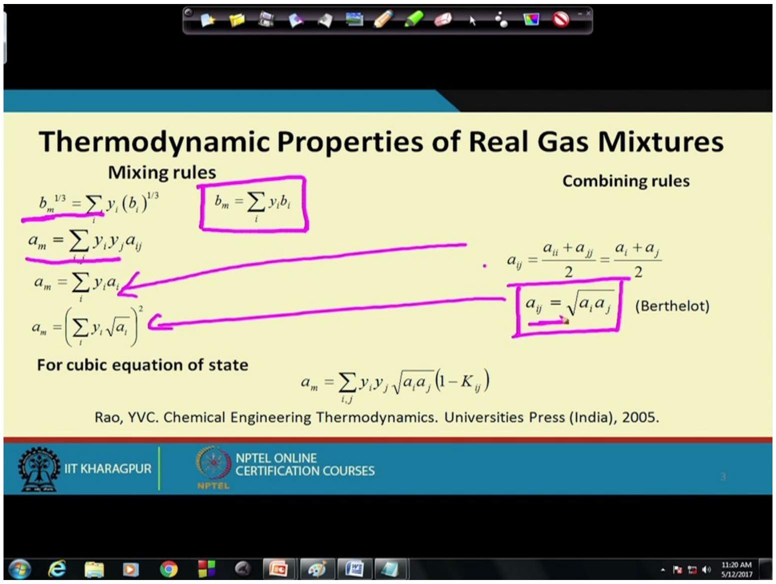

Thermodynamic Properties of Real Gas Mixtures

Mixing rules

$$b_m^{1/3} = \sum_i y_i (b_i)^{1/3}$$

$$\boxed{b_m = \sum_i y_i b_i}$$

$$a_m = \sum_{i,j} y_i y_j a_{ij}$$

$$a_m = \sum_i y_i a_i$$

$$a_m = \left(\sum_i y_i \sqrt{a_i}\right)^2$$

Combining rules

$$a_{ij} = \frac{a_{ii} + a_{jj}}{2} = \frac{a_i + a_j}{2}$$

$$\boxed{a_{ij} = \sqrt{a_i a_j}}$$ (Berthelot)

For cubic equation of state

$$a_m = \sum_{i,j} y_i y_j \sqrt{a_i a_j}\left(1 - K_{ij}\right)$$

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

Now usually the combining rules which we use for a is either to assume that it is an arithmetic mean of the component is or to assume that it is a geometric mean of the component a's. When we assume the arithmetic mean then we come across this particular equation and when we use the geometric mean we come across this particular equation. Usually the trend is to assume the geometric mean this has been used by Van der waals himself, it was first proposed by Berthelot and then we find that although it was empirical London could proposed some theoretical justification for it so that nowadays we are quite convinced with it.

And I would also like to mention that it is not only (a) which is expressed in terms of such a geometric mean in fact any parameter of thermodynamics which gives mixture interaction in terms of component interaction is often expressed in terms of such an expression as aij. So therefore we find out that for any cubic equation of state this is not only for Van der waals equation of state for any cubic equation of state usually we will find that b is expressed by this equation and a is expressed in terms of this equation.

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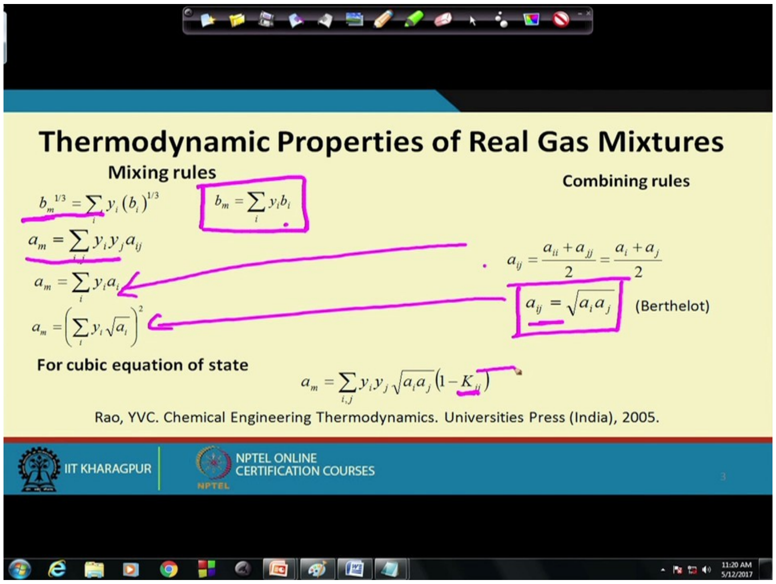

Thermodynamic Properties of Real Gas Mixtures

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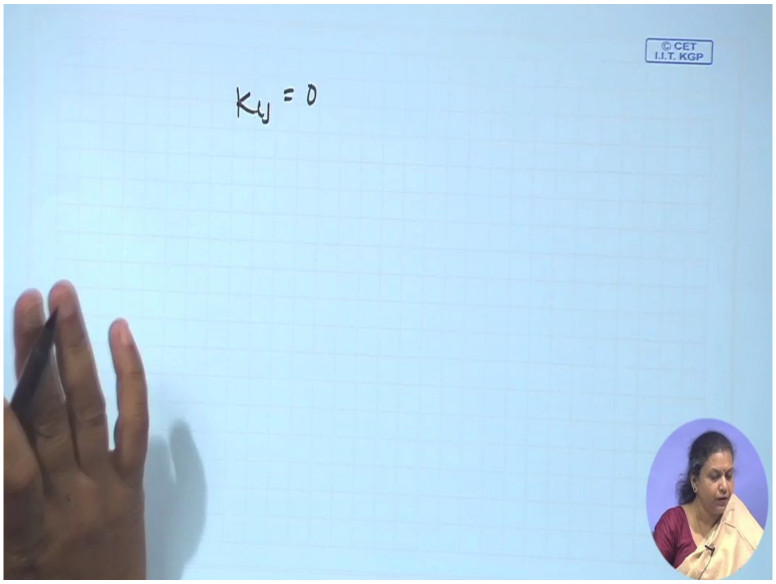

Now here we find that that we have introduced a parameter Kij. Kij it is nothing but it is the binary interaction parameter between components i and j. It arises due to the binary interaction it is simply adopted for a better prediction between experiments and theory and for most of the purposes we will find that we take kij equals to 0. It is just adopted for whenever there is good amount of mismatch between experiment and theory.

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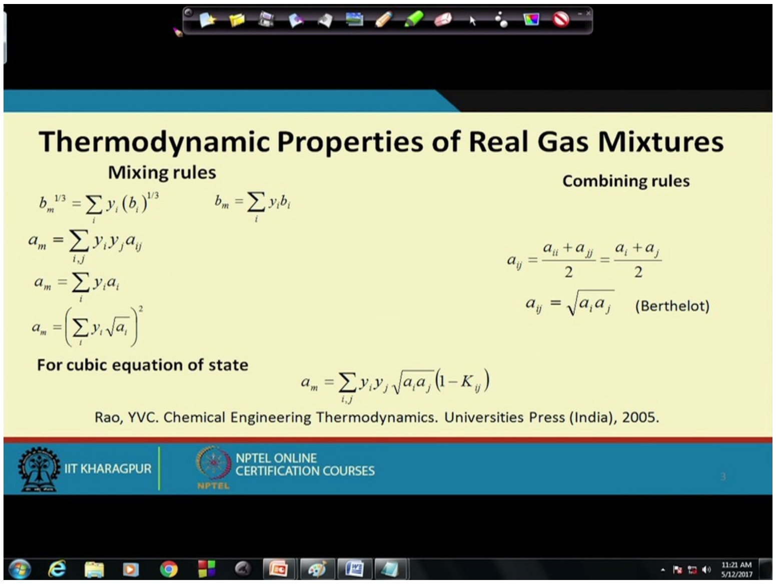

Thermodynamic Properties of Real Gas Mixtures

Mixing rules

$$b_m^{1/3} = \sum_i y_i (b_i)^{1/3} \qquad b_m = \sum_i y_i b_i$$

$$a_m = \sum_{i,j} y_i y_j a_{ij}$$

$$a_m = \sum_i y_i a_i$$

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Combining rules

$$a_{ij} = \frac{a_{ii} + a_{jj}}{2} = \frac{a_i + a_j}{2}$$

$$a_{ij} = \sqrt{a_i a_j} \quad \text{(Berthelot)}$$

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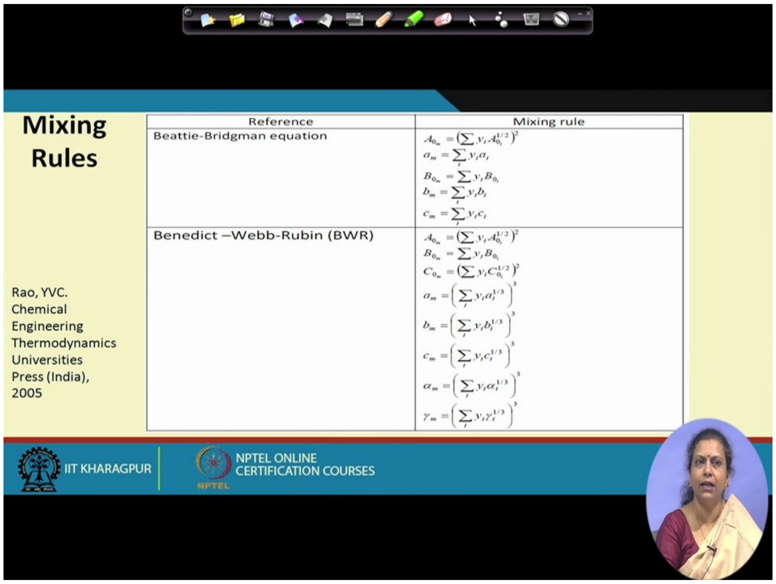

Mixing Rules

Reference	Mixing rule
Beattie-Bridgman equation	$A_{0_m} = (\sum y_i A_{0_i}^{1/2})^2$ $a_m = \sum_i y_i a_i$ $B_{0_m} = \sum y_i B_{0_i}$ $b_m = \sum_i y_i b_i$ $c_m = \sum_i y_i c_i$
Benedict –Webb-Rubin (BWR)	$A_{0_m} = (\sum y_i A_{0_i}^{1/2})^2$ $B_{0_m} = \sum y_i B_{0_i}$ $C_{0_m} = (\sum y_i C_{0_i}^{1/2})^2$ $a_m = \left(\sum_i y_i a_i^{1/3}\right)^3$ $b_m = \left(\sum_i y_i b_i^{1/3}\right)^3$ $c_m = \left(\sum_i y_i c_i^{1/3}\right)^3$ $\alpha_m = \left(\sum_i y_i \alpha_i^{1/3}\right)^3$ $\gamma_m = \left(\sum_i y_i \gamma_i^{1/3}\right)^3$

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

So therefore when we are dealing with cubic equation of state we find that we can adopt the mixing rules which has been written down here. Now let me tell you that there are several other mixing rules also which have been proposed it is quite natural because we really we do not know which mixing rule is going to help under what condition. So therefore there are large, whatever number of equations of state are there almost for each of the cases there are equivalent number of mixing rules, so these are some additional mixing rules which we find.

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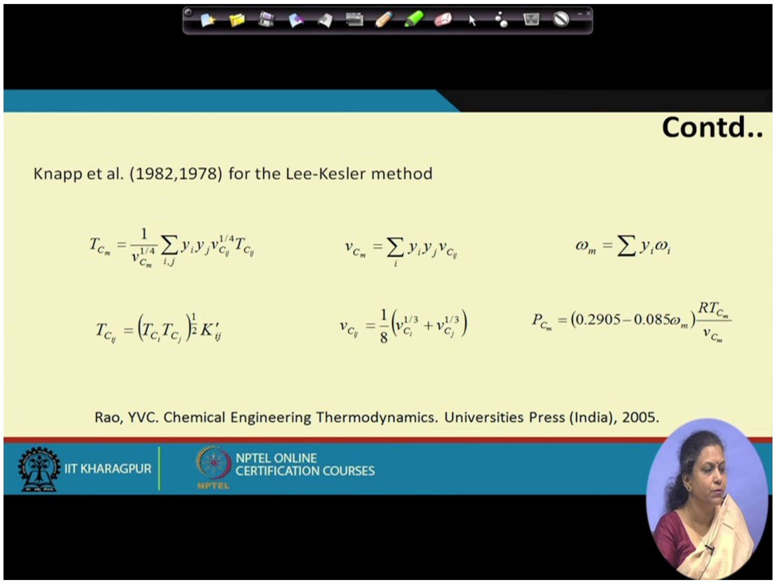

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Knapp et al. (1982,1978) for the Lee-Kesler method

$$T_{C_m} = \frac{1}{v_{C_m}^{1/4}} \sum_{i,j} y_i y_j v_{C_{ij}}^{1/4} T_{C_{ij}} \qquad v_{C_m} = \sum_{i} y_i y_j v_{C_{ij}} \qquad \omega_m = \sum y_i \omega_i$$

$$T_{C_{ij}} = \left(T_{C_i} T_{C_j}\right)^{\frac{1}{2}} K'_{ij} \qquad v_{C_{ij}} = \frac{1}{8}\left(v_{C_i}^{1/3} + v_{C_j}^{1/3}\right) \qquad P_{C_m} = (0.2905 - 0.085\omega_m)\frac{RT_{C_m}}{v_{C_m}}$$

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And then we find that in these particular mixing rules we find that the critical constants should also be expressed, so therefore again for these mixing rules some particular mixing rules for the critical constants TCm, VCm and PCm all those things have been suggested. Equivalent mixing rules are also available for virial equation of state where also we find that there are mixing rules and combining rules taken into account, the mixture property in terms of pure component property and also the interaction parameter in terms of pure component interaction parameters.

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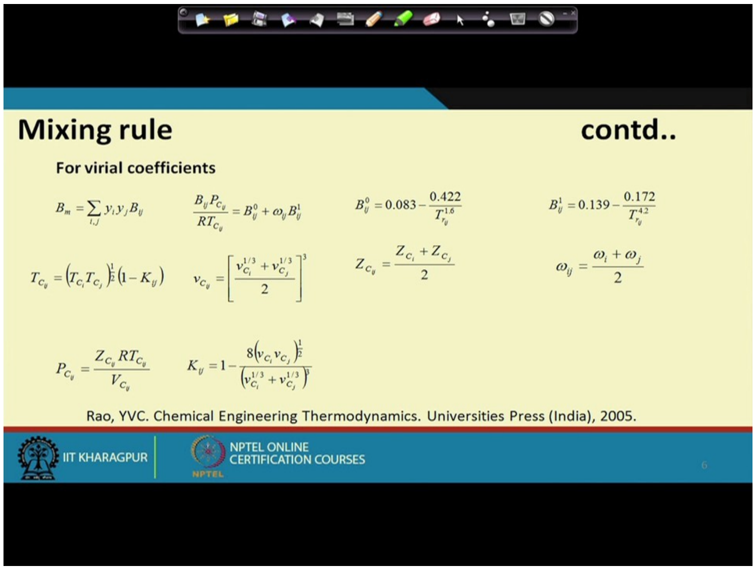

Mixing rule **contd..**

For virial coefficients

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

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

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

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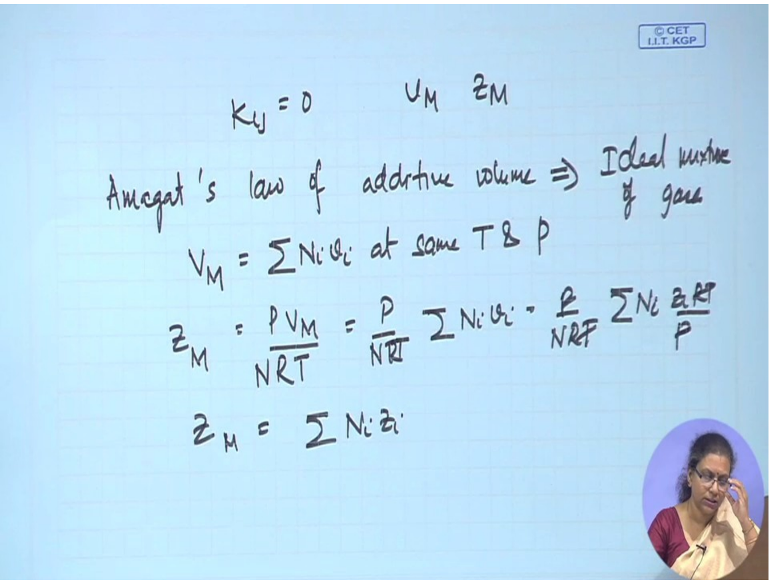

$k_{ij} = 0 \qquad v_M \quad z_M$

Amagat's law of additive volume $\Rightarrow$ Ideal mixture of gases

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

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

$$z_M = \sum N_i z_i$$

So accordingly we find that in this particular case also we have proposed your this bM has been written and then this bM has to be expressed in terms of B ig, so Bij is taking the 3 parameter law of corresponding states which is expressed in this particular term where Bij0 Bij1 these are expressed as shown here.

But again you must remember that all these equations they are empirical in nature, right? Now apart from these also we find that in most of the equations we need to know vM and we need to know zM that we have already seen, so apart from the cubic equation and virial equation of state there is another way also by which we can find this out these are by assuming Amagat's law of additive volume and Dalton's law of additive pressure.

What do these equations say? These equations say for example this equation it simply says that V mixture is nothing but equal to Nivi since in this particular case we assume that vi refers to the molar volume of each and every component this is primarily applicable to, it is not an ideal mixture of gases, right? So therefore in this particular case how can we express zM as? This is nothing but equal to PvM by NRT, correct?

Can we not write it down as P by NRT Sigma Nivi VM has been substituted by this or in other words this can also be written down as P by NRT Sigma NI ziRT by P. I have replaced each particular vi with ziRT by P. So therefore from here what do I get? I get zM is nothing but equal to Nizi. We continue our discussions with Amagat's law of additive volume and Dalton's law of partial pressure in the next class and once we wind up with the mixing rules and the combining rules for the different equations of state we will go to some more interesting and important properties of mixtures, thank you very much.