Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
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Lecture No 44
Non Ideal Solutions(Contd.)

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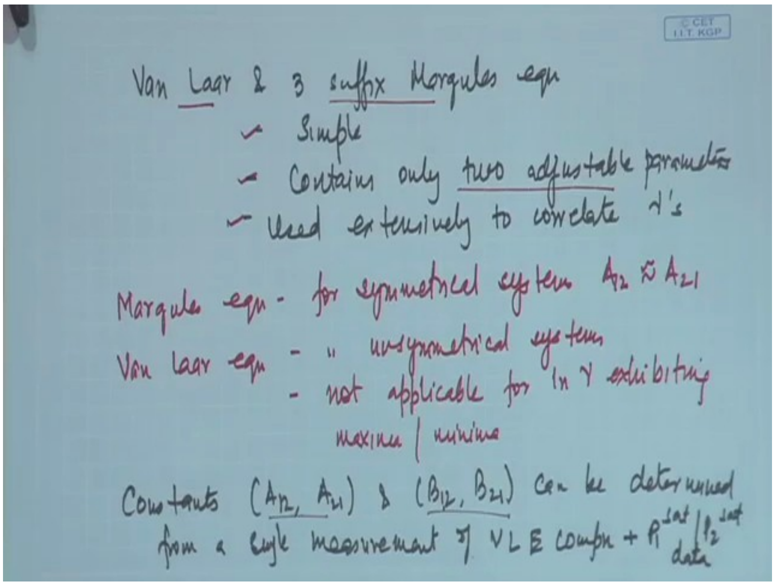

Van Laar & 3 suffix Margules eqn

✓ Simple

✓ Contains only two adjustable parameters

✓ Used extensively to correlate γ's

Margules eqn - for symmetrical system $A_{12} \approx A_{21}$

Van laar eqn - " unsymmetrical system

- not applicable for $\ln \gamma$ exhibiting maxima / minima

Constants (A_{12}, A_{21}) & (B_{12}, B_{21}) can be determined from a single measurement of VLE compn + P_1^{sat} / P_2^{sat} data

Well to continue our discussions on nonideal solutions or more specifically on the van laar and the 3 suffix Margules equation we were trying to find out, how to find out activity coefficients using these 2 before I start I would like to mention once more that both the van laar and the 3 suffix Margules equation they are firstly simple they contain only 2 adjustable parameters and they are used extensively to correlate gammas.

Now amongst these 2 it is important for you to remember that Margules equation it is usually used for symmetrical systems when A12 is almost equal to A21 and Van laar equation it is used usually for unsymmetrical systems these are just as guides as when you should apply which one and it is also important for you to remember that van laar equation although it is used for un-symmetrical systems it is not applicable for ln gamma exhibiting Maxima or minima under this condition van laar equation is not applicable, right?

And we find that since both of these equations this van laar and 3 suffix Margules they contain only 2 adjustable parameters. So therefore we find that the constants which are nothing but A12 and A21 in one case or the B12 and B21 in the other case they can be determined from a single measurement from a single measurement of VLE composition plus P1 saturated, P2 saturated data, so we will we are we will be doing a few problems shortly to just to show you how from a single measurement of VLE composition along with either the Antoine constant or data on saturated vapor pressure of component1 and 2.

Just for a single measurement we can find out these constants, we can find out these constants as a result of which we can generate gamma values using either the van laar or the 3 suffix Margules equation, right?

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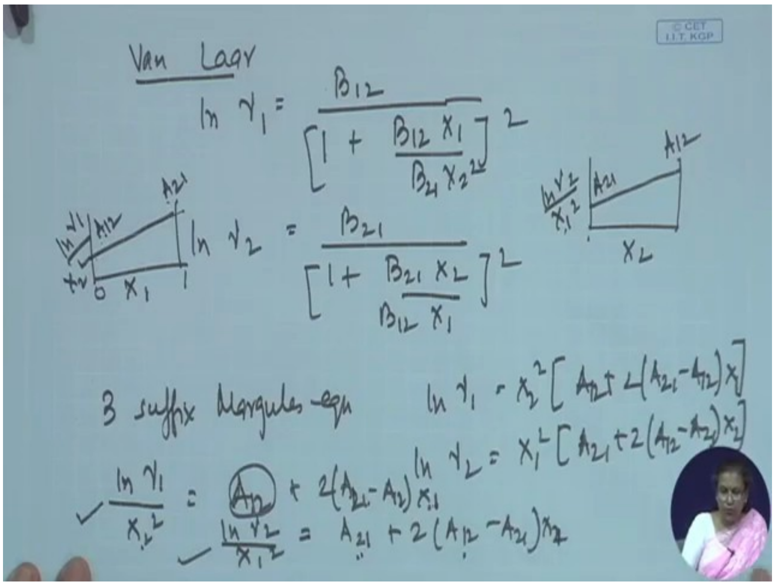

Van Laar

$$\ln \gamma_1 = \frac{B_{12}}{\left[1 + \frac{B_{12} x_1}{B_{21} x_2}\right]^2}$$

$$\ln \gamma_2 = \frac{B_{21}}{\left[1 + \frac{B_{21} x_2}{B_{12} x_1}\right]^2}$$

3 suffix Margules eqn

$$\ln \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12}) x_1]$$

$$\ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21}) x_2]$$

$$✓ \quad \frac{\ln \gamma_1}{x_2^2} = \boxed{A_{12}} + 2(A_{21} - A_{12}) x_1$$

$$✓ \quad \frac{\ln \gamma_2}{x_1^2} = A_{21} + 2(A_{12} - A_{21}) x_2$$

Now coming back to our original discussion, what did we find out in that particular case? We had written down the van laar and the 3 suffix Margules equation in a term which will be friendly or rather in a form where we can find out the constants very easily. So we found out that if we write down the 3 suffix Margules equation in this particular form then we find that that more or less ln gamma1 by X2 square should be linear with X1 and from the intercepts at the 2 extreme positions of X1 equals to 0 and X1 equals to 1 we should be in a position to find out 2 constants, right?

Same thing applies for gamma 2 ln gamma2 by X1 also. Now I had given you a problem if you remember that it's always possible that A12 A21 determined from this particular graph may not be same as the A12 A21 determined from this particular graph. So therefore under that condition what do we do? We try to combine ln gamma1 and ln gamma2 and try to generate a single equation from where we can find out A12 and A21.

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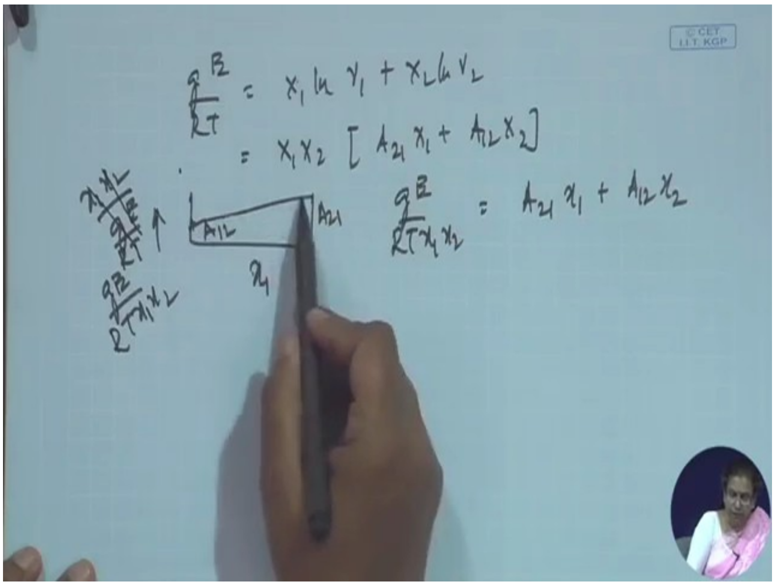

What is the way of combining ln gamma1 ln gamma2? If you recall the original expression of g by RT, what was it? g by RT was equal to if you remember it is nothing but X1 ln gamma1 plus X2 ln gamma2, isn't it? So what can we do for this particular case? We can write it down as if you substitute the expressions of ln gamma1, ln gamma2 then in that case we find that this will be equal to X1X2 A21 X1 plus A12 X2, right?

And from there we find that if we have combined these than in that case we can plot your suppose we plot gE by RT, X1 X2then what do we have suppose we are plotting it in terms of X1 g by g by RT X1 X2 this whole thing taken on this particular site. So in that case what do we have? We have a single equation from which we can find out A12 and A21 just from the 2 extremes.

So therefore this gives us A12, this gives us A21 an average A12 and A21 constituting the variation of both gamma1 and gamma 2 with composition, right? So what do we do from here? We can if we have one data on X1Y1 etc and then from one set of data we can find out these 2, we will be doing a problem shortly.

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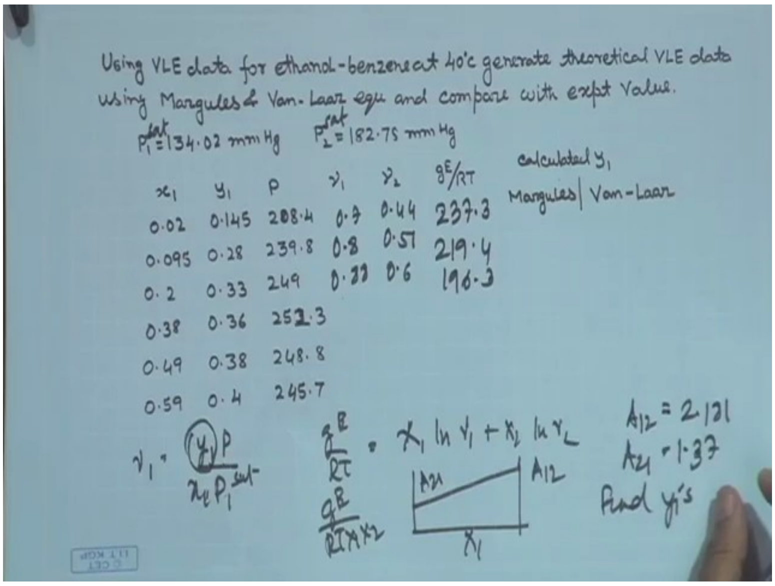

Using VLE data for ethanol-benzene at 40°c generate theoretical VLE data using Margules & Van-Laar equ and compare with expt Value.

$P_1^{sat} = 134.02$ mm Hg $P_2^{sat} = 182.75$ mm Hg

x_1	y_1	P	γ_1	γ_2	g^E/RT	Calculated y_1 Margules | Van-Laar
0.02	0.145	208.4	0.7	0.44	237.3	
0.095	0.28	239.8	0.8	0.51	219.4	
0.2	0.33	249	0.77	0.6	196.3	
0.38	0.36	252.3				
0.49	0.38	248.8				
0.59	0.4	245.7				

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^{sat}}$$

$$\frac{g^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

$$\frac{g^E}{RT x_1 x_2}$$

$A_{12} = 2.121$
$A_{21} = 1.37$
Find y_1's

And once or rather I can show you the problem in this particular case it is a ethanol it is ethanol benzene problem at 40 degrees centigrade you are required to generate theoretical VLE data, say for example you are you are required to use the 3 suffix Margules equation. You know P10 or rather you know P1 saturated you know P2 saturated you have data on X1 you have data on P, right? And you’re supposed to find out the y1 values using Margules equation as well as van laar equation which we will discuss shortly.

And then you need to compare with the experimental data, fine. So therefore you already know P1 saturated P2 saturated, now from here what do we know? You can find out gamma1 equals which is y1P by x1 P1 saturated. So therefore you can find out the individual gammas in this particular case for example say for instance the gammas in this particular case it will be something of this sort you can check it up and can find out.

The corresponding gamma 2’s also can be found out and once you have, so how do you find out gamma 2 and gamma 1? You are first supposed to find out gE by RT by X1X2, so what do you do? Once you know these things you can find out gamma 1 gamma 2 and then from there you can find out gE by RT as sorry X1 ln gamma1 plus X2 ln gamma 2 then you know the gE by RT for what did different X1 Y1 values?

For example in this case it’s about say 237.3, 219.4, 196.3 and so on and so forth. You can just calculate once you have calculated this then what do you do? You simply plot gE by RT X1 X2 as a function of the different X1s that you have. You find out the straight line and from this particular straight-line you find out A21 and A12 once A21 and A12 have been found out then from there you can generate the gamma values for the different compositions and once you have done that then you can find out y1 for each case and you can compare with the experimental y1 values, right?

So therefore this is the way that that you are supposed to work out in this particular case. We know that for just check up you will be finding A12 into is particular case as 2.181, A21 will be 1.37, so once you know them you find yis or y1s whatever it is and then you can proceed and you can find it out, fine. So this was about the Margules equation.

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Now what about the van laar equation, just look at the van laar equation the way I have written down. In this case what do you expect? How do you expect to proceed in the for the case of van laar equation.

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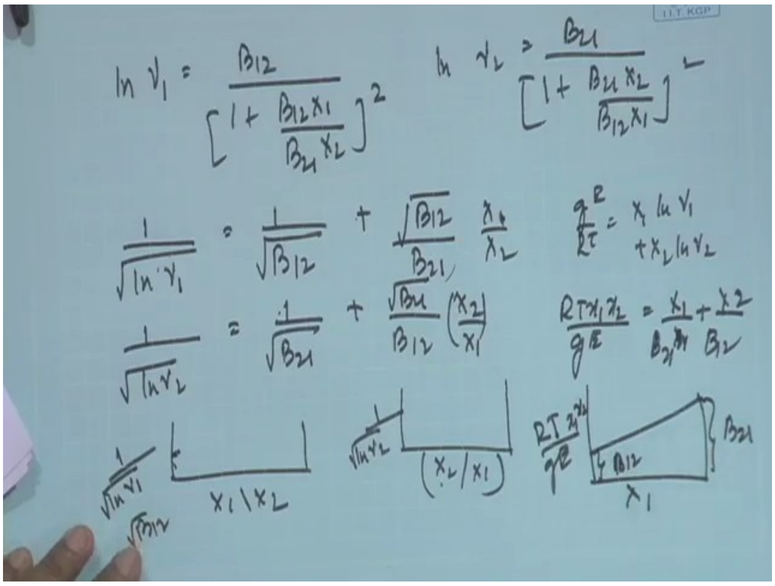

So in this particular case just look at the equation, can we write it down in this form? Say suppose if we can write it down as ln gamma1 which is equal to I will just write down the equation once more it was B12 by 1 plus B12 X1 by B21 X2 whole square and this was ln gamma 2 it was B21 by 1 plus B21 X2 by B12 X1 whole square. Just these 3 equations it will be good if you can remember them, agreed? So therefore can we just write it down in this particular form?

Just check up, if you can do it in this particular form root B12 by B21 X1 by X2 and same way one by root ln gamma2 this will be 1 by root B21 plus root b21 by B12 X2 by X1, right?

So in this particular case what can we do? We can plot 1 by root ln gamma 1 as a function of X1 by X2 and then from there we can find out from the slope and the intercept. Similar way we can plot out one by root ln gamma2 as a function of X2 by X1.

And then from both of these we know that the slope in this particular case it is going to be or in other words we know that at X1 equals to 0 the intercept here will be root B12 and at X1 and so therefore from here we can find it out and again from here we can find out B21 again there is a problem that from the slope and intercept the values that we have got they might be different when they are using this equation or this graph and this graph, so what we need?

We need a proper averaging or a proper summation using the g by RT value, right? So for this case again suppose we use gE by RT equals to X1 ln gamma1 plus X2 ln gamma 2 then what you find in this particular case? You find that suppose we plot RT X1 X2 by gE then in that case this will be equal to 1 by B21 X1 plus 1 by B12, sorry B12 this X1 is here this is X2, right? So therefore in this particular case if we plot RT X1 X2 by gE as a function of X1 then we find that we get a straight line is intercept here will be B12 and intercept here will be B21.

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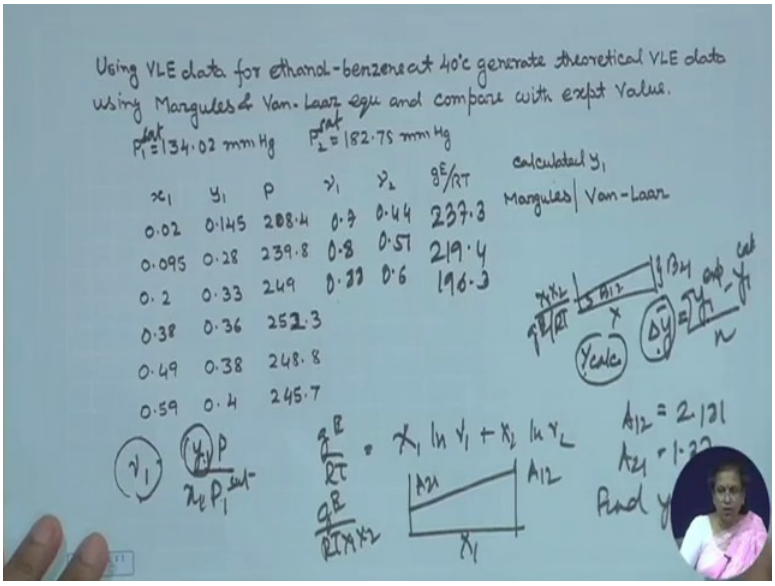

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$\gamma_1 = \frac{y_1 P}{x_1 P_1^{sat}}$

$\frac{g^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$

$A_{12} = 2.131$

So therefore in a very similar manner if we take up this particular data. Here in this particular case also you can very well from here again find out gamma 1 gamma 2 gE by RT is the same then instead of this particular thing in, here you need to plot X1 X2 by gE by RT as a function of X1 and then from the intercepts you are in a position to find out B12 and B21, once you found them out then from there you can find out the gammas from the gammas you can find out y1 and you can compare with the results in this particular case.

So you can try out this problem and you can find out the, what are the more or less how comparable you find the experimental data with the calculated data that you find and then in and you can compare the thing which you need to do is you need to find out y calculated, okay. And then once you find out y calculated for each case then in that way the variation can be found out from Delta y bar equals to yi experiment minus yi calculated the Sigma of the whole thing divided by n.

So you are required to find out this thing this Delta ybar for 3 suffix Margules and for van laar compare the 2 and then you can comment on the suitability of the 2 equations.

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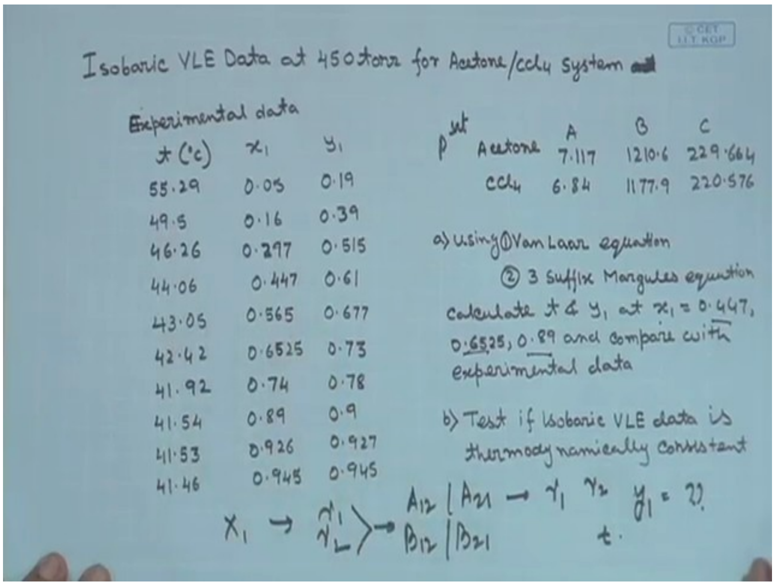

Isobaric VLE Data at 450 torr for Acetone/CCl_4 System

Experimental data

t (°c)	x_1	y_1
55.29	0.05	0.19
49.5	0.16	0.39
46.26	0.277	0.515
44.06	0.447	0.61
43.05	0.565	0.677
42.42	0.6525	0.73
41.92	0.74	0.78
41.54	0.89	0.9
41.53	0.926	0.927
41.46	0.945	0.945

P^{sat}	A	B	C
Acetone	7.117	1210.6	229.664
CCl_4	6.84	1177.9	220.576

a) Using ① Van Laar equation
② 3 Suffix Margules equation
Calculate t & y_1 at $x_1 = 0.447$, 0.6525, 0.89 and compare with experimental data

b) Test if Isobaric VLE data is thermodynamically consistent

$X_1 \to \left.\begin{matrix}\gamma_1 \\ \gamma_2\end{matrix}\right\rangle \to \begin{matrix}A_{12} | A_{21} \\ B_{12} | B_{21}\end{matrix} \to \gamma_1 \ \gamma_2 \quad y_1 = ?? \quad t.$

In the similar way there is also one more problem you can take it up the previous problem it had given you data it was an isotherm thermal data, here we have got a Acetone\CCl_4 mix system and we are providing you isobaric VLE data and in this case the P1 and P2 saturated are not provided the Antoine’s constants are provided from which you can find out the P saturated for Acetone and P saturated for CCl_4.

And then if you’re using van laar equation and 3 suffix equation in the same way you can find out the constants A12 A21, constants B12 B21 once you know those particular constants we assume that they do not vary with temperature as a result of which at X1 at these 2 values you can find out when you know the X1 from there you can find out gamma 1. You can you already you have found out gamma 1 gamma 2 using this particular data.

And then from these gamma 1 gamma 2 you can find out A12 A21 in the other case you can find out B12 B21, once is particular thing is available then you can find out gamma 1 for any particular condition gamma 2 for any particular condition and from there you can find out y1 equals to and then once you know y1 you know everything you can find out temperature and you are supposed to compare with experimental data and find out how accurate it is.

So this is a general way by which we find out the activity coefficients we can use the 2 suffix Margules equation when the situation when it is not very far removed from ideality when it is slightly more removed we slightly modify the 2 suffix Margules equation and try to use the 3 suffix Margules or the van laar equations. For the purpose of the class it is sufficient for you to be involved with these 3 types of equations for the other equations it is just important to know when we use the other equations.

For example Wilson's plot or rather Wilson's equation it is used when there is a temperature dependence of the constants are quite significant the NRTL is used when the 2 particular components they are not randomly mixed and so on and so forth. But for this particular class we will be concerned with 2 suffix Margules equation, 3 suffix Margules equation and the van laar equation.

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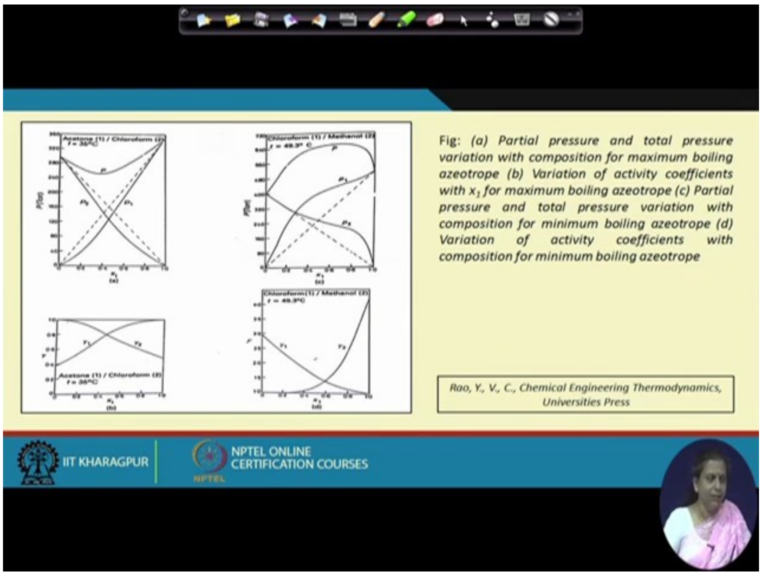

Fig: *(a) Partial pressure and total pressure variation with composition for maximum boiling azeotrope (b) Variation of activity coefficients with x_1 for maximum boiling azeotrope (c) Partial pressure and total pressure variation with composition for minimum boiling azeotrope (d) Variation of activity coefficients with composition for minimum boiling azeotrope*

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Now apart from this I would also like to mention one more interesting thing. When there is a remarkable or significant deviation of the solution from ideal behaviour, what do you expect under that condition? Let us see what happens. For that particular condition we find that whether it is a negative deviation or positive deviation we find that see the curve has to start from sorry the curve it has to start from P1 P2 saturated it has to end to P1 saturated. Now when there is significant deviation from ideality then in that case we find that very frequently the curve it either passes through maxima when there is positive deviation from Raoult's law or it can pass through minima when there is a negative deviation from Raoult's law, under this condition what happens?

When there is such a significant deviation from Raoult's law we find that there is either a maxima or a minima and if we plot the corresponding temperature curves we find that in those particular TX plots also we find that the temperature or the boiling point of the mixture will be either much greater than the boiling point of the individual components or it will be less as compared to the boiling point of the individual components. So accordingly we find that at this particular point where we encounter a maxima in the PX curve for example here or we encounter minima in the Py curve, what do we find?

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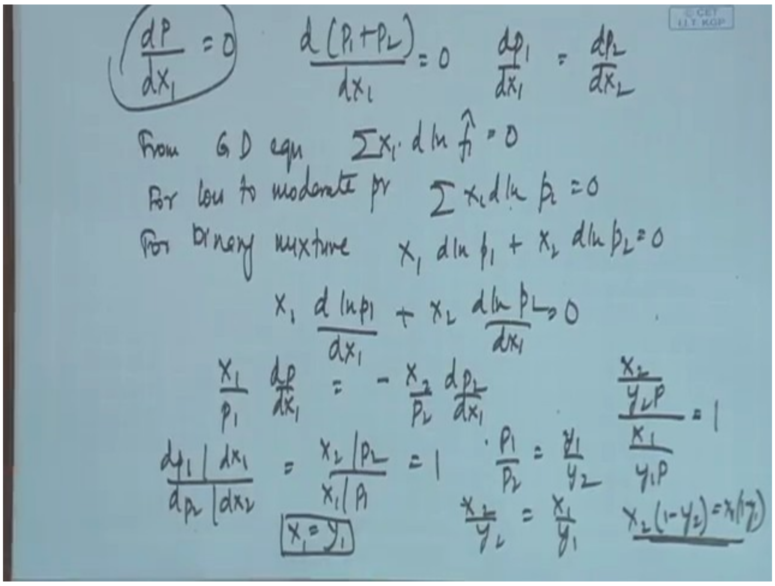

$\boxed{\frac{dP}{dx_1}=0}$ $\frac{d(P_1+P_2)}{dx_1}=0$ $\frac{dp_1}{dx_1}=\frac{dp_2}{dx_2}$

From G D eqn $\sum x_i \, d\ln\hat{f}=0$

For low to moderate pr $\sum x_i \, d\ln p_i=0$

For binary mixture $x_1 \, d\ln p_1 + x_2 \, d\ln p_2=0$

$x_1 \frac{d\ln p_1}{dx_1} + x_2 \frac{d\ln p_2}{dx_1} = 0$

$\frac{x_1}{p_1}\frac{dp}{dx_1} = -\frac{x_2}{p_2}\frac{dp_2}{dx_1}$

$\frac{dp_1/dx_1}{dp_2/dx_2} = \frac{x_2/p_2}{x_1/p_1} = 1$ $\frac{P_1}{P_2}=\frac{y_1}{y_2}$ $\frac{x_2/y_2P}{x_1/y_1P}=1$

$\boxed{x_1=y_1}$ $\frac{x_2}{y_2}=\frac{x_1}{y_1}$ $x_2(1-y_2)=x_1(y_1)$

That for this particular situation can we not write down dP by dX1 equals to 0. What is this P? It is just the summation of the partial pressures, so therefore we can write it down in this particular way. From where we can write down dP1 d X1 is nothing but equal to dP2 d X2, agreed? From Gibbs Duhem equation what do we know? Just remember one thing repeatedly during our entire discussion on ideal as well as nonideal.

Particularly for nonideal solution for everything we are coming back to Gibbs Duhem equation. So that shows the significance of this equation as far as phase equilibrium thermodynamics is concerned. From Gibbs Duhem equation what do we know in terms of fugacity? One more thing I would like to mention we are using Gibbs Duhem equation either in terms of chemical potential or in terms of fugacity or in terms of activity coefficient just to find out some data when other data are known or to test thermodynamic consistency of VLE data which will be discussing in the next class or maybe to prove certain things which are not very self-evident.

As we will be doing in this particular case, from Gibbs Duhem equation in terms of fugacity we know that the equation is this. This equation from low to moderate pressure what happens? Fugacity becomes partial pressure Pi equals to 0 for binary mixtures or binary solution whatever you say this reduces to X1 d ln P1 plus X2 d ln P2 equals to 0, right? So from here what do we get? We get X1 d ln P1 d X1 plus X2 d ln P2 d X1 equals to 0.

Or in other words can we write it down as X1 by P1 this equals to minus X2 by P2 d P2 dX1, agreed? Or in other words can we write it down as dP1 d X1 by d P2 d X2 equals to X2 by P2 by X1 by P1 this is equal to one. Now what is this P1 by P2 equals to? This P1 by P2 it is nothing but equals to y1 by y2, isn't it? Because it's important to remember that we can substitute this P2s with y2P. So therefore what do we get? We get X2 by Y2P by X1 by Y1P this is equal to one.

From here we get X2 by Y2 equals to X1 by Y1 or X2 into 1 minus Y2 will be X1 into 1 minus Y1 and from this equation what do we get? We get that at the point of Azeotropy where this particular equation is applicable x equals to y or in other words X1 equals to y1 or X2 equals to Y2.

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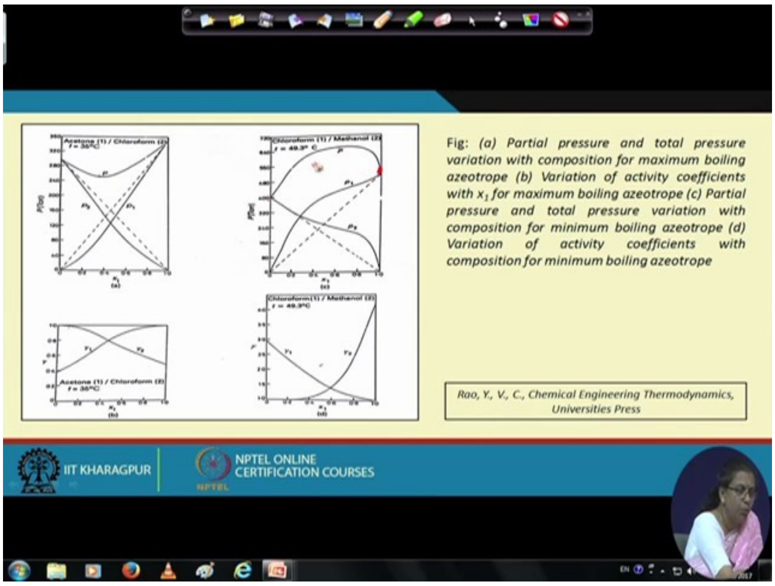

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So therefore what do we find? We find that at the point of Azeotropy definitely there is a maximum or a minimum in the pressure versus X1 plot. When there is a maximum quite naturally the boiling point of the solution under this particular condition it will naturally be less as compared to the boiling point of the pure components, so therefore for positive deviation of Raoult's law, what do we get?

We get a minimum boiling mixture in the same way for negative deviation of Raoult's law we find that temperature of boiling point of the solution at the point of minimum pressure will be higher as compared to the boiling point of the pure components. So therefore we are going to get a maximum boiling Azeotrope under this particular condition, fine.

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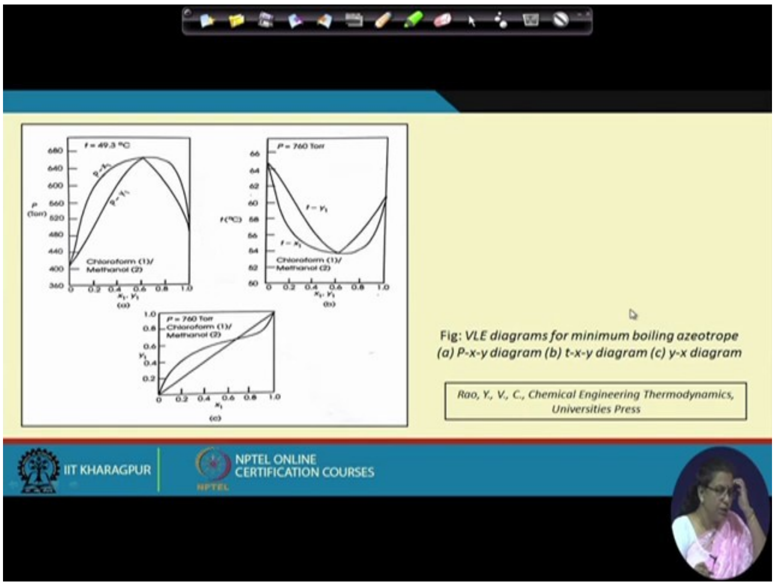

Fig: VLE diagrams for minimum boiling azeotrope (a) P-x-y diagram (b) t-x-y diagram (c) y-x diagram

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And accordingly we find that under these 2 conditions under the conditions of your minimum boiling Azeotrope for positive deviation we have a minimum boiling Azeotrope and at this particular sorry at this particular condition we find that there is a maximum in the pressure curve there at this particular condition the boiling point is much less as compared to the boiling point of the pure component. And for this particular condition we find that the equilibrium curve it coincides with the diagonal line as a result of which X equals to Y under this condition.

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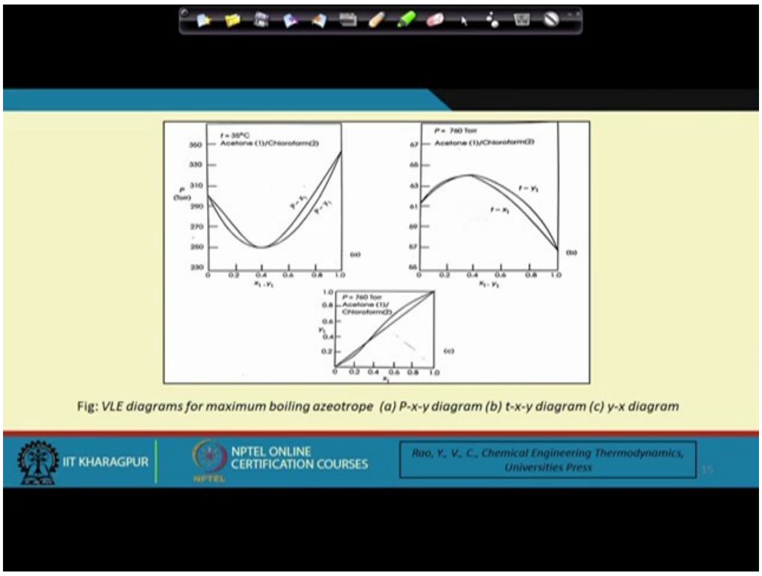

Fig: VLE diagrams for maximum boiling azeotrope (a) P-x-y diagram (b) t-x-y diagram (c) y-x diagram

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In the similar way we find that when there is a negative deviation from Raoult's law under that condition what do we find for negative deviation from Raoult's law we have a maximum boiling mixture for maximum boiling Azeotrope and here also it is X1 equals to Y1 under this condition.

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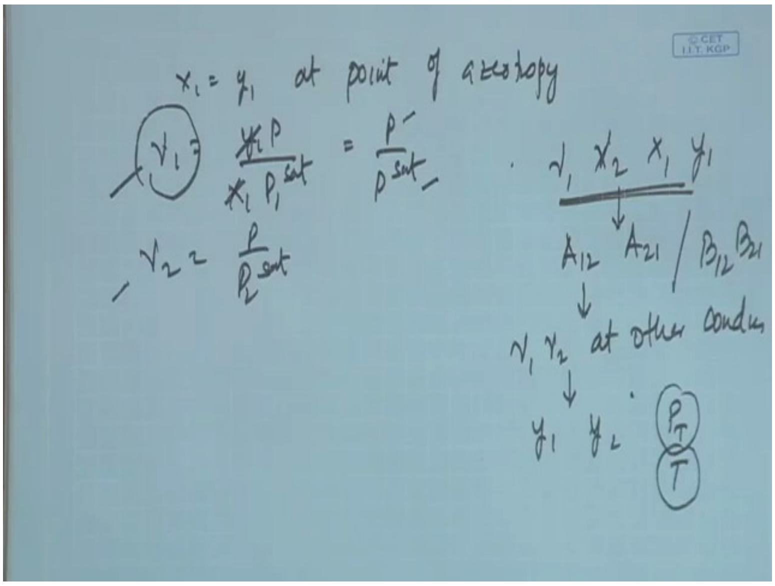

Now this gives you a very fortunate situation what do we know? We know that X1 equals to Y1 at point of Azeotropy, right? What is gamma1 equals to can you tell me? It is Y1P by X1 P1 saturated, when X1 and y1 are same that in that case gamma1 it is simply equal to P by P saturated. So therefore you see that when there is a large deviation from Raoult’s law and we actually encounter Azeotropes be the maximum or a minimum Azeotrope we find that gamma 1 at the point of Azeotropy can be obtained as a ratio of the total pressure and the saturated pressure of that component.

This is gamma 1 this is gamma 2, so once at the point or once we can locate the point of Azeotropy we can find out gamma 1 and gamma 2 at that particular point then for these 2 points once at the point of Azeotropy gamma 1 and gamma 2 can be found out and we have selected a proper excess Gibbs free energy model it can be either Van laar or Margules. So therefore if we know gamma we know X gamma 1 gamma 2, we know X1 we know we know y1 at the point of Azeotropy then we should be in a position to find out either A12 A21 or B12 B21 depending upon the model that we have selected and once we can find this out then from these we can find out gamma 1, gamma 2 at other conditions from which we can find out Y1Y2 if P is not given then P if T is not given then T under that particular condition, right?

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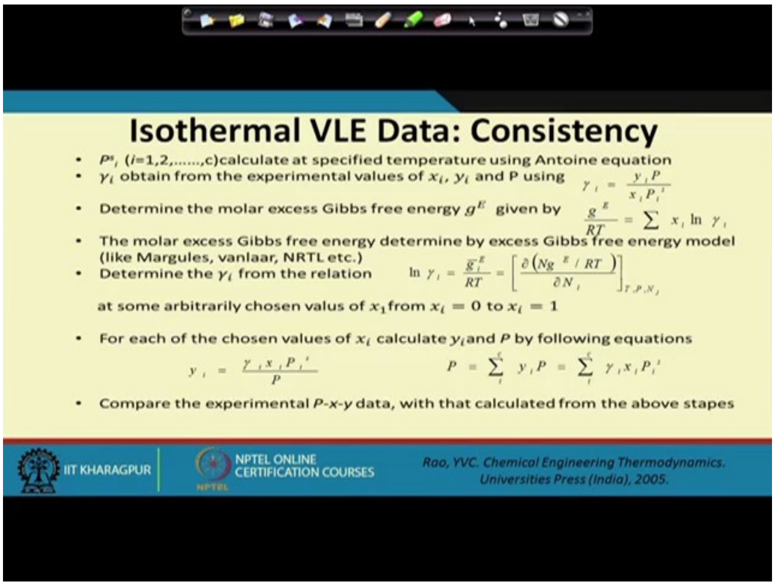

Isothermal VLE Data: Consistency

- $P^s{}_i$ (i=1,2,.......,c)calculate at specified temperature using Antoine equation
- γ_i obtain from the experimental values of x_i, y_i and P using $\gamma_i = \frac{y_i P}{x_i P_i^s}$
- Determine the molar excess Gibbs free energy g^E given by $\frac{g^E}{RT} = \sum x_i \ln \gamma_i$
- The molar excess Gibbs free energy determine by excess Gibbs free energy model (like Margules, vanlaar, NRTL etc.)
- Determine the γ_i from the relation $\ln \gamma_i = \frac{\bar{g}_i^E}{RT} = \left[\frac{\partial (Ng^E / RT)}{\partial N_i}\right]_{T,P,N_j}$

  at some arbitrarily chosen valus of x_1 from $x_i = 0$ to $x_i = 1$
- For each of the chosen values of x_i calculate y_i and P by following equations

  $$y_i = \frac{\gamma_i x_i P_i^s}{P} \qquad P = \sum_i^c y_i P = \sum_i^c \gamma_i x_i P_i^s$$
- Compare the experimental P-x-y data, with that calculated from the above stapes

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

So therefore the calculations become pretty simple under these conditions and I have just jotted down, they will be doing a few more problems on 2 suffix Margules equation and the under conditions of Azeotropy these problems are pretty simple and they will be doing a few of them in your assignments and if you have further doubts regarding these problems you are always welcome to ask us during our either you can upload the questions and we will be glad to answer those questions.

Now here I would like to show you the rather I have just jotted down the methodology which is used in order to solve the vapor liquid equilibrium problems under isothermal conditions.

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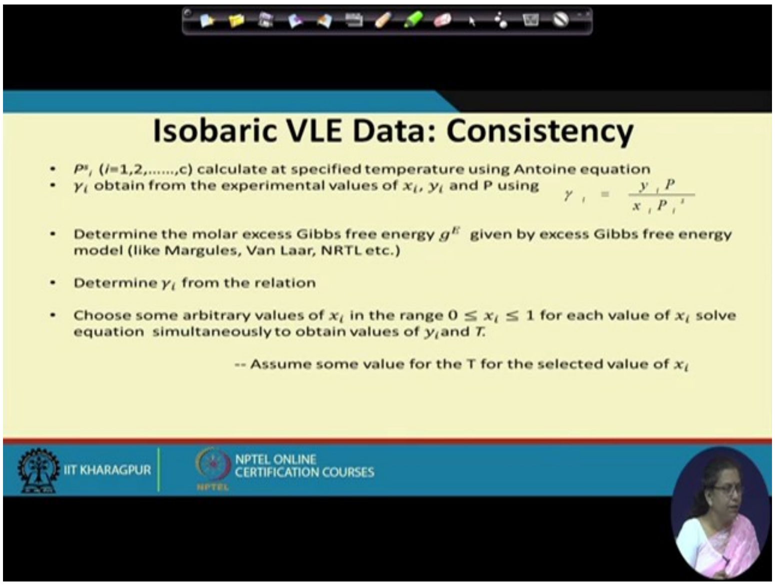

Isobaric VLE Data: Consistency

- P^s_i (i=1,2,......,c) calculate at specified temperature using Antoine equation
- γ_i obtain from the experimental values of x_i, y_i and P using $\gamma_i = \frac{y_i P}{x_i P_i^s}$
- Determine the molar excess Gibbs free energy g^E given by excess Gibbs free energy model (like Margules, Van Laar, NRTL etc.)
- Determine γ_i from the relation
- Choose some arbitrary values of x_i in the range $0 \le x_i \le 1$ for each value of x_i solve equation simultaneously to obtain values of y_i and T.

-- Assume some value for the T for the selected value of x_i

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Under isobaric conditions.

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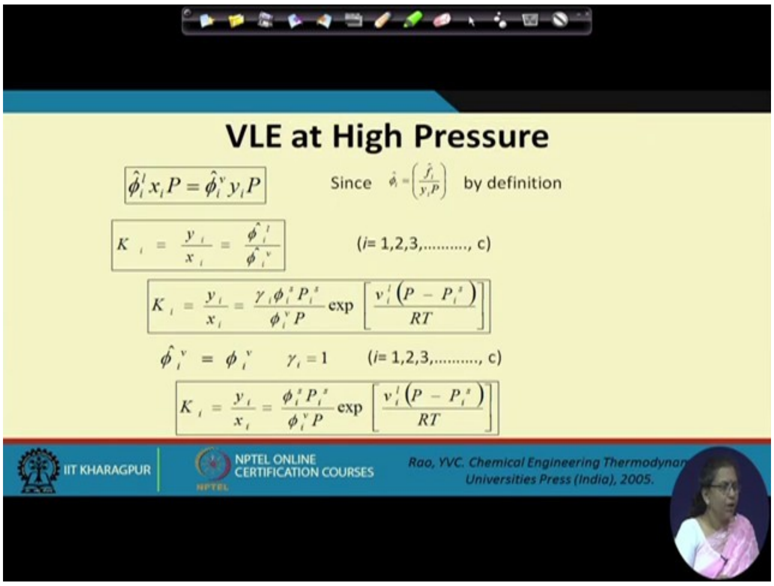

VLE at High Pressure

$$\boxed{\hat{\phi}_i^l x_i P = \hat{\phi}_i^v y_i P}$$

Since $\hat{\phi}_i = \left(\frac{\hat{f}_i}{y_i P}\right)$ by definition

$$\boxed{K_i = \frac{y_i}{x_i} = \frac{\hat{\phi}_i^l}{\hat{\phi}_i^v}} \qquad (i = 1,2,3,\ldots\ldots\ldots, c)$$

$$\boxed{K_i = \frac{y_i}{x_i} = \frac{\gamma_i \phi_i^s P_i^s}{\phi_i^v P} \exp\left[\frac{v_i^l (P - P_i^s)}{RT}\right]}$$

$$\hat{\phi}_i^v = \phi_i^v \qquad \gamma_i = 1 \qquad (i = 1,2,3,\ldots\ldots\ldots, c)$$

$$\boxed{K_i = \frac{y_i}{x_i} = \frac{\phi_i^s P_i^s}{\phi_i^v P} \exp\left[\frac{v_i^l (P - P_i^s)}{RT}\right]}$$

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

And also at high pressure, now at high pressure what happens? We cannot replace fugacity with pressure under this condition. So therefore for these particular conditions more or less usually when we are dealing with hydrocarbons what we do is we try to express Ki in terms of yi and xi. And we find that this particular Ki this accounts for the non-ideality in the liquid phase it accounts for the non-ideality in the vapor phase and very frequently several Ki plots have been suggested for hydrocarbons.

We are in a position to rather you will be in a position to find out the plots and so therefore yeah, just I will be undoing it I will be doing it once more.

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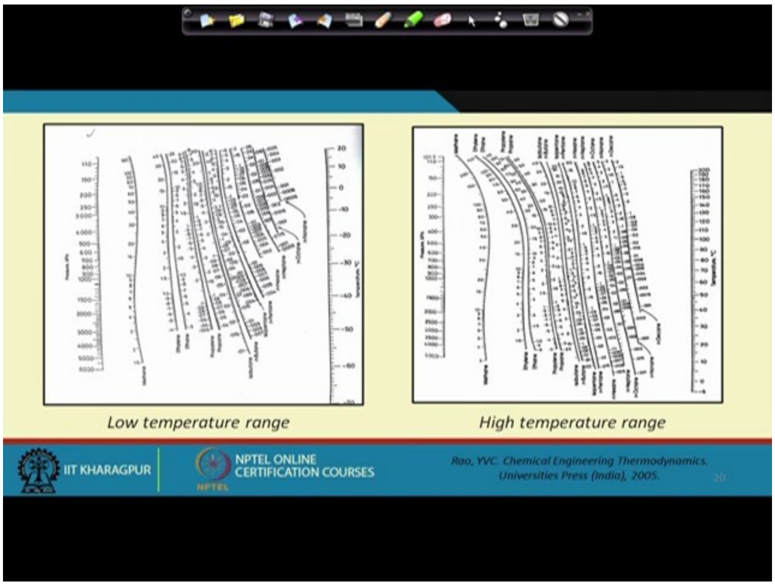

Low temperature range

High temperature range

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Yeah, so several K plots are available for different pressure and temperature conditions at low-temperature range and high-temperature range from which K can be found out and the VLE at high pressure can be worked out accordingly.

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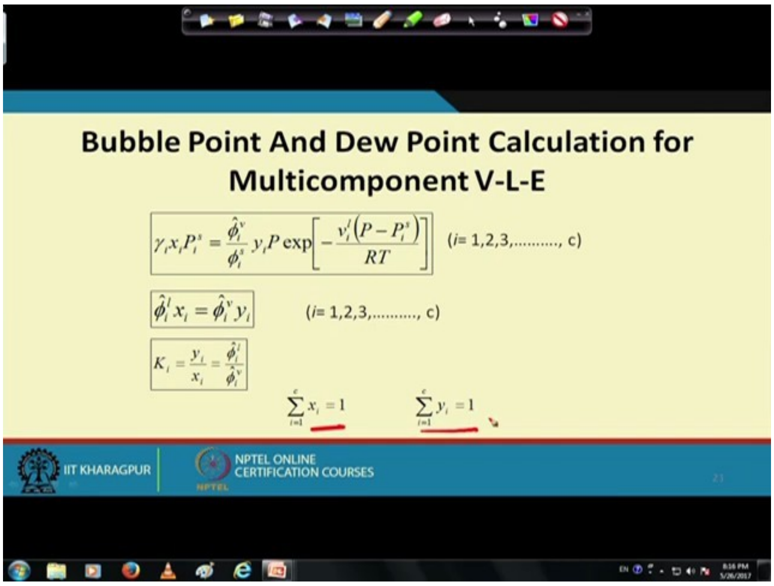

Bubble Point And Dew Point Calculation for Multicomponent V-L-E

$$\boxed{\gamma_i x_i P_i^s = \frac{\hat{\phi}_i^v}{\phi_i^s} y_i P \exp\left[-\frac{v_i^l\left(P-P_i^s\right)}{RT}\right]} \quad (i = 1,2,3,\ldots\ldots\ldots., c)$$

$$\boxed{\hat{\phi}_i^l x_i = \hat{\phi}_i^v y_i} \quad (i = 1,2,3,\ldots\ldots\ldots., c)$$

$$\boxed{K_i = \frac{y_i}{x_i} = \frac{\hat{\phi}_i^l}{\hat{\phi}_i^v}}$$

$$\underline{\sum_{i=1}^{c} x_i = 1} \qquad \underline{\sum_{i=1}^{c} y_i = 1}$$

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And well the bubble point and dew point calculations we have been discussing for binary mixtures, if you’re going for multi-component VLE data the same procedure is going to apply just we need to remember that instead of working with 2 components we will be working with more than 2 component and for this particular part the determining the for this particular cases we find for this particular cases we find that determining this Sigma Xi equals to 1 and these particular checks are particularly very important for this particular cases, right?

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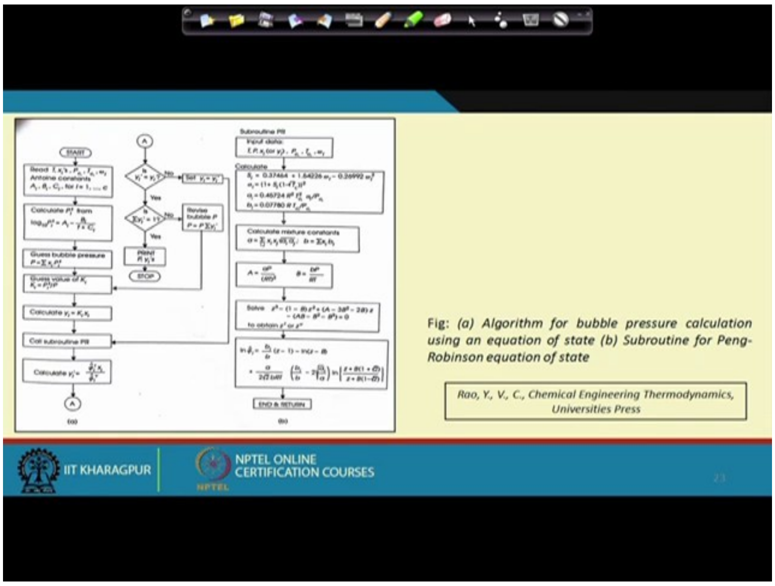

Fig: (a) Algorithm for bubble pressure calculation using an equation of state (b) Subroutine for Peng-Robinson equation of state

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And very frequently what we do in this particle case is that I have written down the algorithm for bubble Pt estimation and also we have we have written down the algorithm when we are using the Peng-Robinson equation of state.

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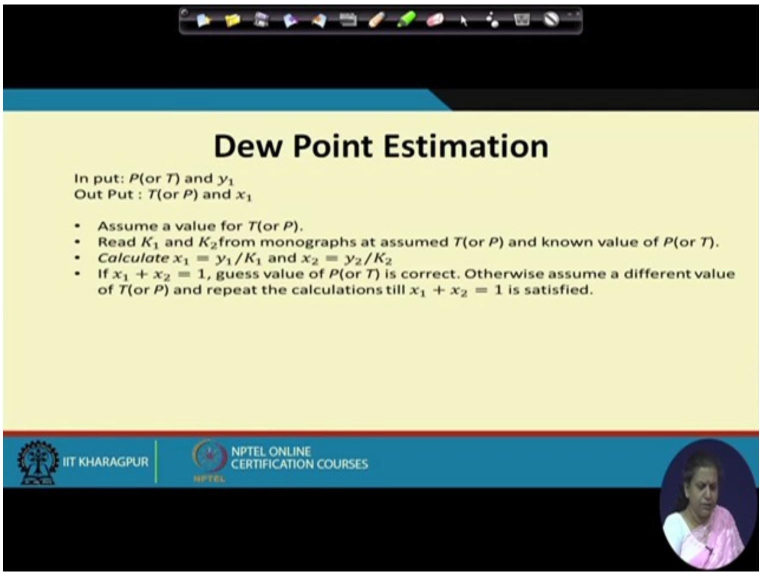

Dew Point Estimation

In put: P(or T) and y_1
Out Put : T(or P) and x_1

- Assume a value for T(or P).
- Read K_1 and K_2 from monographs at assumed T(or P) and known value of P(or T).
- *Calculate* $x_1 = y_1/K_1$ and $x_2 = y_2/K_2$
- If $x_1 + x_2 = 1$, guess value of P(or T) is correct. Otherwise assume a different value of T(or P) and repeat the calculations till $x_1 + x_2 = 1$ is satisfied.

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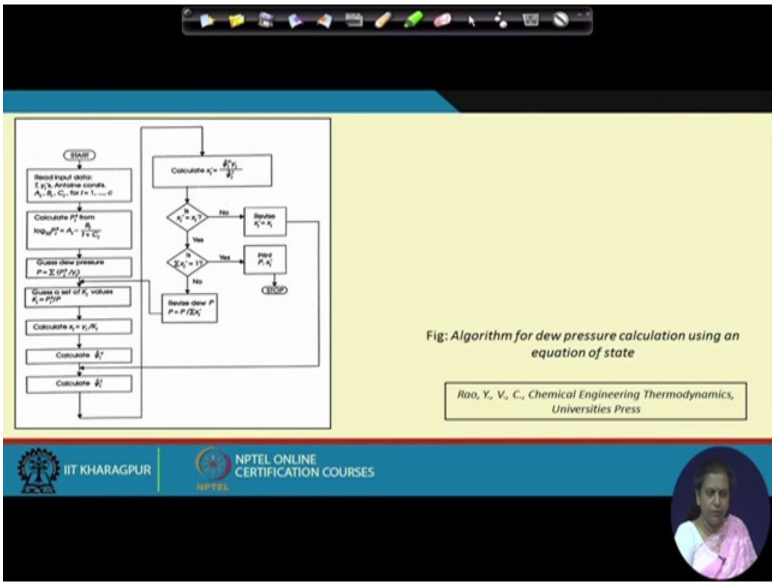

Fig: *Algorithm for dew pressure calculation using an equation of state*

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I have also written down the steps for finding out the dew point estimation the algorithm for finding out the dew point due pressure calculation.

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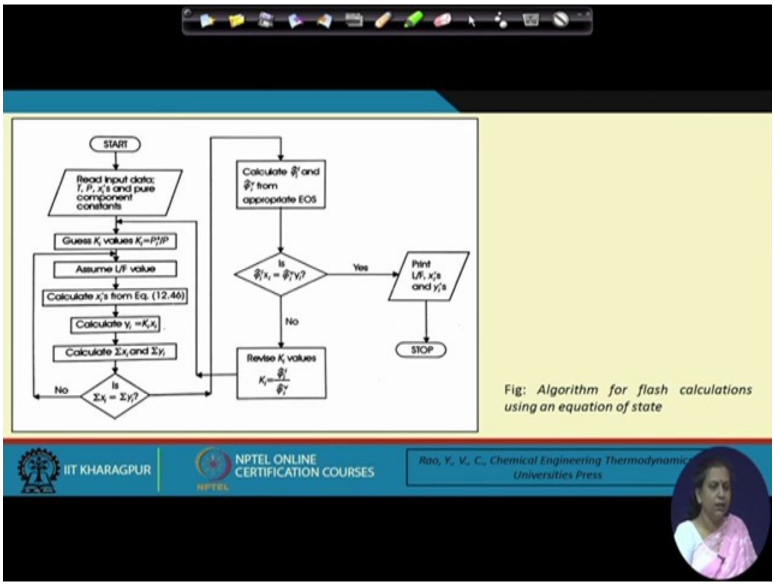

Fig: *Algorithm for flash calculations using an equation of state*

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And also for the Flash calculations, right? So therefore you can use this particular algorithms and you can you can find out the VLE data at high pressure and the VLE data for multi-component system remembering very well that the VLE data at low pressure that has been discussed for binary systems is applicable in this particular case.

When we go for multi-component systems then in that case we have more number of equations, more number of equilibrium relationships and as a result of which with these more number of equations we can find out the different gammas when we are dealing with high pressure instead of pressure we have to have to use fugacity but for this particular class usually we will be concentrating on binary solutions at low to moderate pressure, fine.

And when we know that there is a point of Azeotropy the calculations becomes simpler. For the purpose of this class it will be important for you to remember that we will be primarily considering once more I repeat 2 suffix Margules equation 3 suffix Margules equation and van laar equation of state, thank you very much.