Course on Phase Equilibrium Thermodynamics
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Lecture No 47

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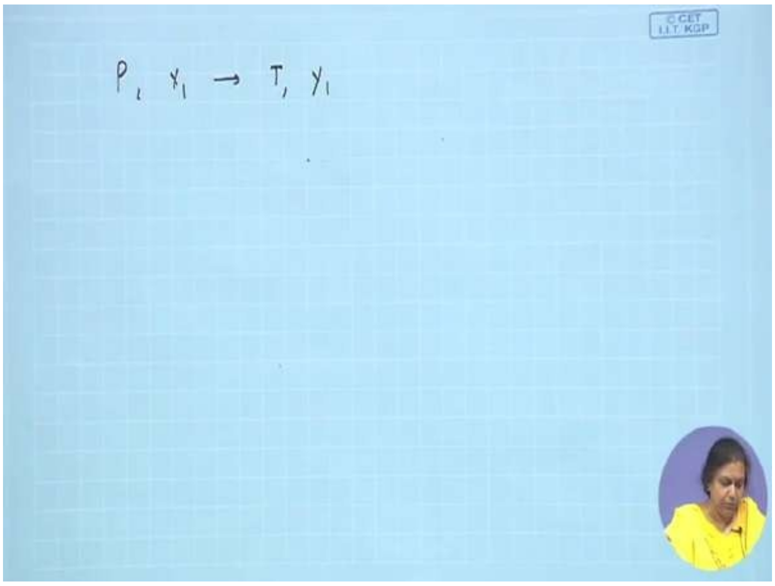

Well, to continue our discussions regarding the isobaric data. Now in this case what do we have? We have P we know P and possibly we know X1 we will be in a, we would be required to find out T and y1 say, right? So therefore in this particular case there is small amount of trial and error which is involved. Now for most of the cases what we do? We assume some particular T for that T is you find out Pi saturated and Pi saturated for the different components.

Once you know Pi saturated you know P, so therefore you will you will be in a position to find out the constants of the of the particular excess Gibbs free energy model that you're going to assume. So from there you find out either A12 or B12 B21, again once you have found them out you are now in a position to find out gamma i for the other conditions, right? And so therefore from that particular gamma i if you know X i and you know yi then you're in a position to find out the P and the mole fractions in the vapor phase.

If you know the mole fractions in the liquid phase you're going to calculate it and going to see whether the constraint that I had mentioned Sigma Xi or Sigma yi equals to 1 it depends on what you're finding out. Are you finding out the liquid phase composition or the vapor phase composition? Find out the compositions for each of the component and see if the composition adds up to 1. If it adds up to 1 your temperature assumption was correct if it does not go for a different temperature assumption. The direction in which your assumption should proceed will be obvious once you find out whether your Sigma Xi is greater than one or less than one.

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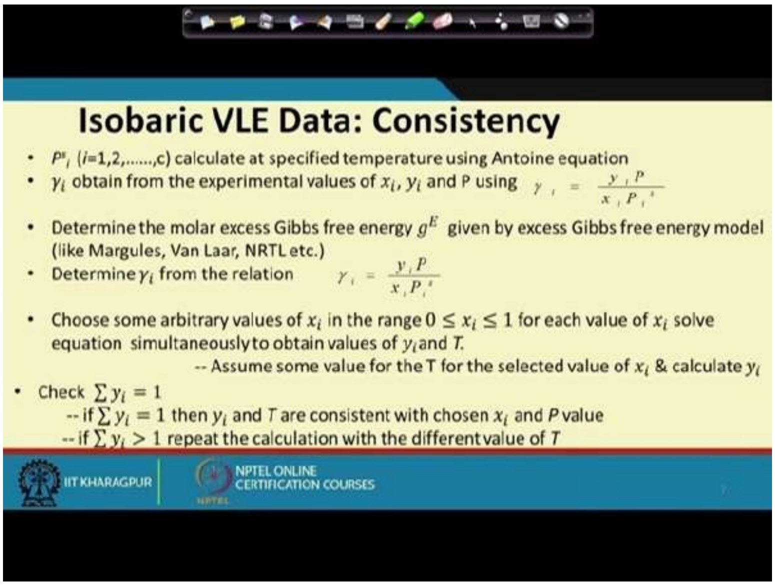

The methodology of for finding it out is mentioned in this particular slide but unless we take up a specific problem this is not going to be clear to you.

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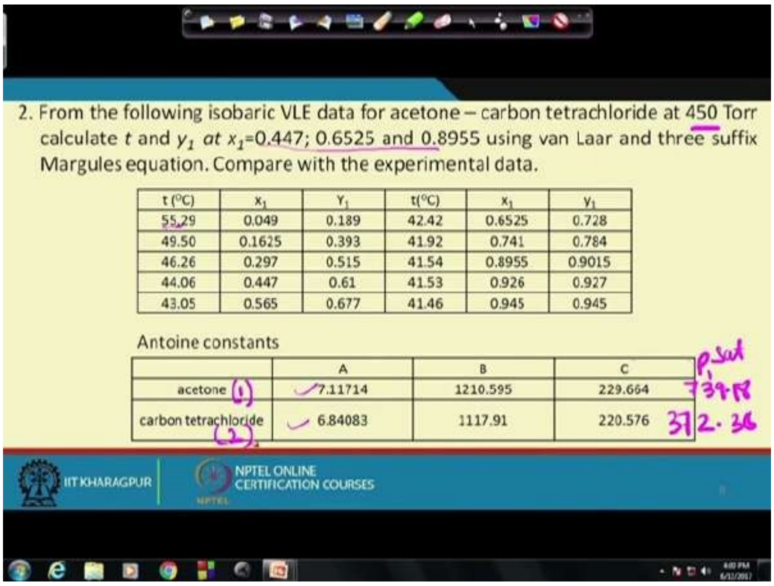

So therefore we go for a second problem here. This is an acetone carbon tetrachloride mixture it’s almost the same as the previous one, just the previous one was an isothermal data this was an isobaric data. You’re supposed to use both van laar as well as the 3 suffix Margules equation and you're supposed to find out t and y1 your P is is given here it is 450Torr and the X1s for 3 different X1s you're supposed to find it out.

In this way also the way we proceed it is alright. The small amount some fragmentary data is given, so based on this fragmentary data you can take up this 55.29. Once you know t degree centigrade you know the Antoine constants for acetone for carbon tetrachloride. So from here you are in a position to find out Pi saturated. You find that for acetone it is 739.18Torr and for CCl_4 it is 372.36Torr, right?

So therefore these 2 you have found out and obviously here in this case also you find that acetone has a higher saturated vapor pressure and we designate this as component 1 and we designate this as component 2.

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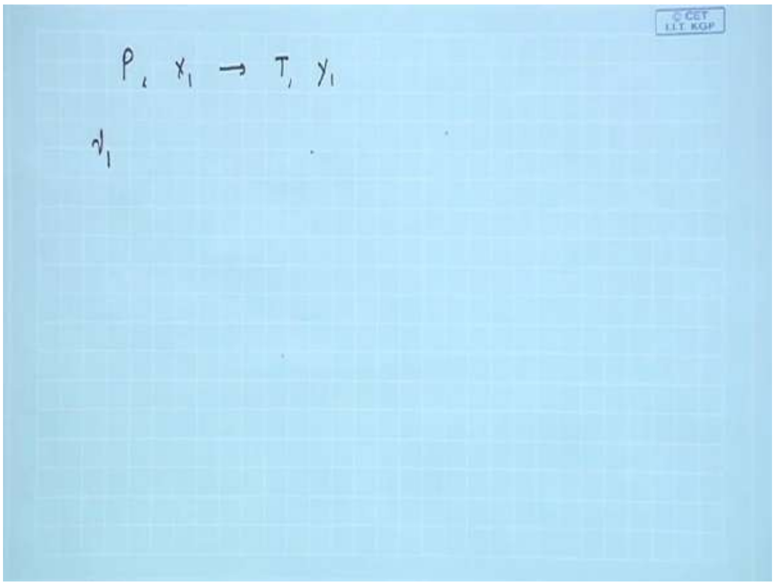

So now once we have found out these now we are in a position to find out gamma 1.

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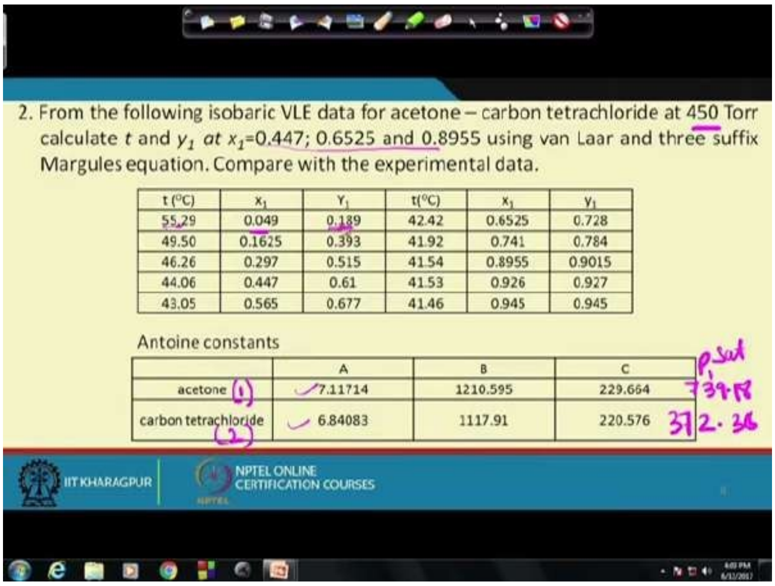

For the first condition let us say X1 equals to 0.049 y1 equals to 0.189.

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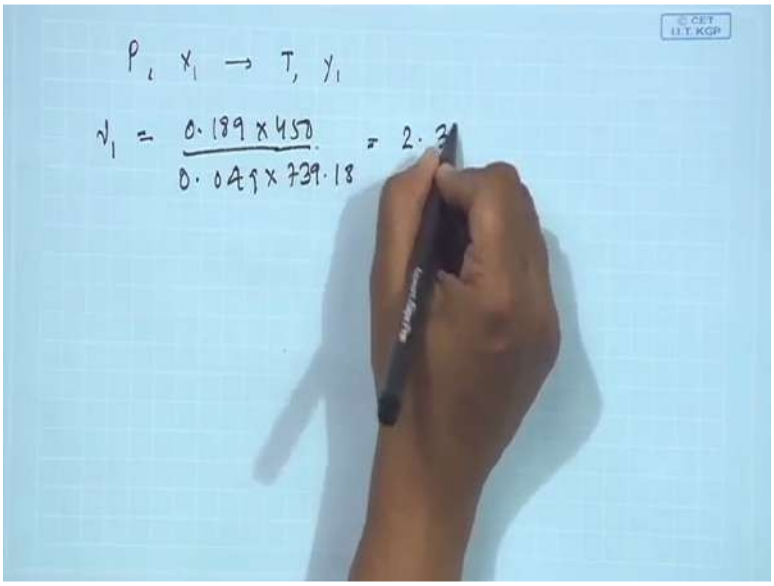

So therefore for this particular condition we can find out gamma 1 it is 0.189 into 450Torr divided by 0.049 into739.18, the P saturated gamma 1 it is 2.3482. Same way you can find out gamma 2 0.811 into 450 by 0.951 into 372.36 this becomes 1.0306. Same approach as we have done the previous problem this is X1 ln gamma 1 plus X2 ln gamma 2 this particular case this is 0.0705.

Now suppose we start dealing with the van laar equation of state. For the van laar equation of state what we get? We need to plot your x1 x2 by gE by RT its not a big deal you can calculate it. It’s going to be 0.6610.

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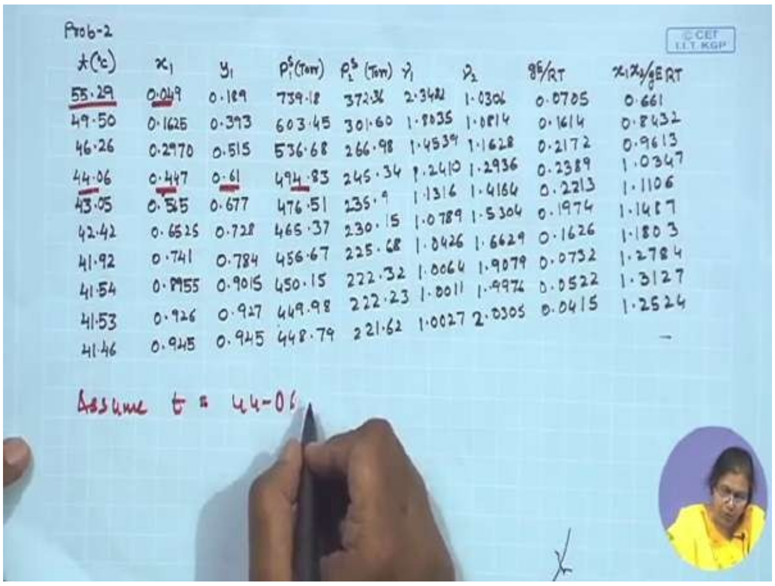

Now once this is calculated then you can repeat this particular calculation for other conditions as well, right? So in this particular table I have written down all the calculations which have been made the just the I have demonstrated the calculations for one particular data for this particular data I have demonstrated the calculations for other data the calculations are going to be the same. So this is the total table for the entire calculations that I have performed. Once this has been done then from here you can find out you are required to find out X1 as 0.447. So for this case y1 P1 saturated everything can be obtained experimentally.

Now we have to find out theoretically, how to do it? Once you know this x1 x2 by this particular value. So therefore initially let us assume some t, let us assume the t which is already provided here which is 44.06. So we can assume t equals to 2 44.06 X1 is 0.447.

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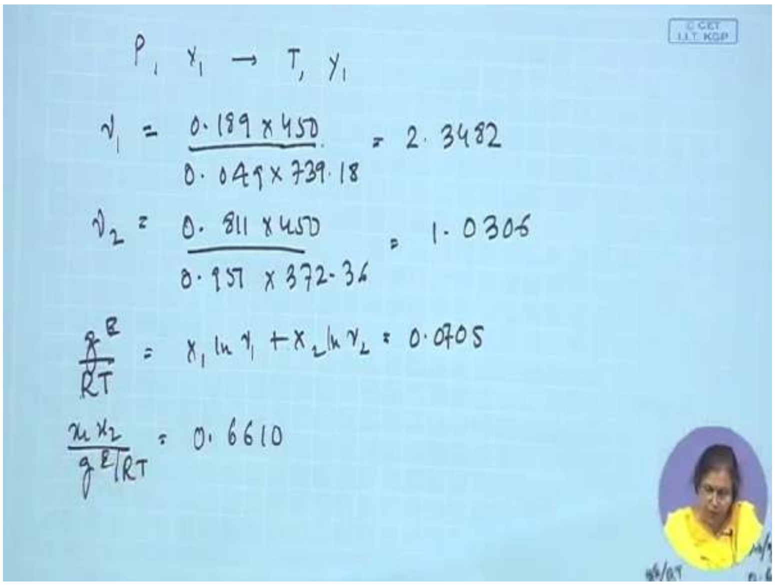

Gamma 1 we have we have already found out it is 1.24 and gamma 2 equals to 1.28 these things we have already found already found out from here the gamma1 and gamma 2 values.

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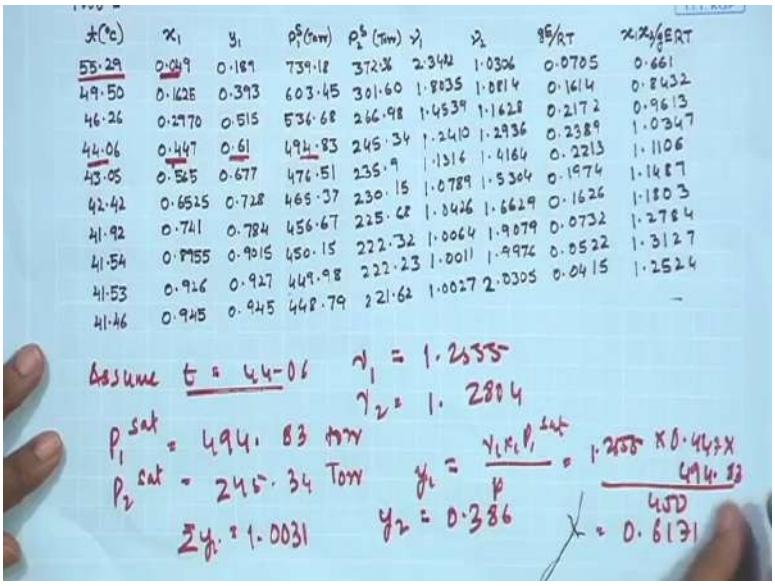

So therefore from here we are in a position to find out that for this particular case gamma1 is equal to it is equal to 1.2555 gamma 2 equals to 1.2804, right? So if we assume t equals 44.06 we arein a position to find out p1 saturated which is nothing but equal to 494.83Torr, P2 saturated you can find out 245.34Torr from which you can find out y1 it is just gamma1 X1 P1 saturated by P. So it is 1.2555 into 0.447 into 494.83 divided by450 equals to 0.6171.

Accordingly y2 it's equal to 0.386 add up y1 and y2 it's 1.0031 you can take this as more or less close to one. If you want to go for slightly better values then in that case you have to again change t. Now you know that since Sigma y1 is greater than one you should reduce the t in this particular case.

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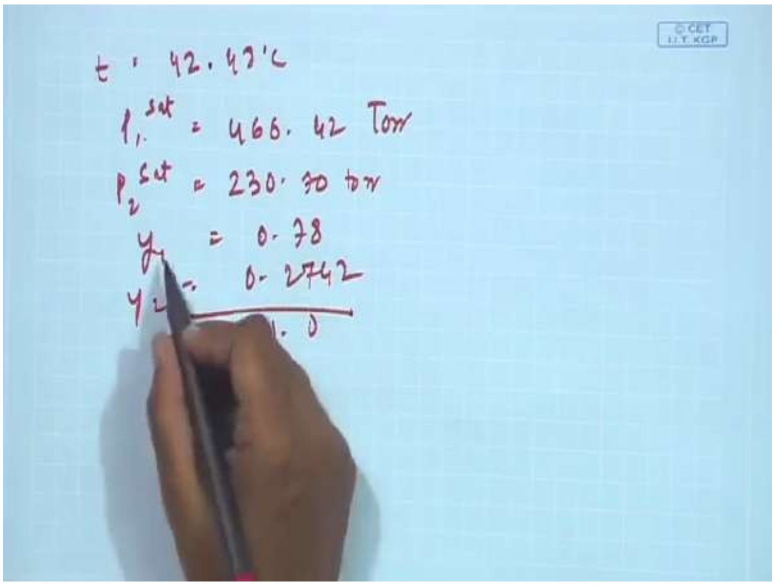

So let us go for a second assume t. Let us take this second assume t say as t equals to 42.48 degrees centigrade. Find out P1 saturated, 466.42Torr, P2 saturated 230.70Torr, y1 you can find it out, again y2 you can find it out add the 2 you get more or less Sigma yi equals to 1. So therefore this is your assumed thing is correct.

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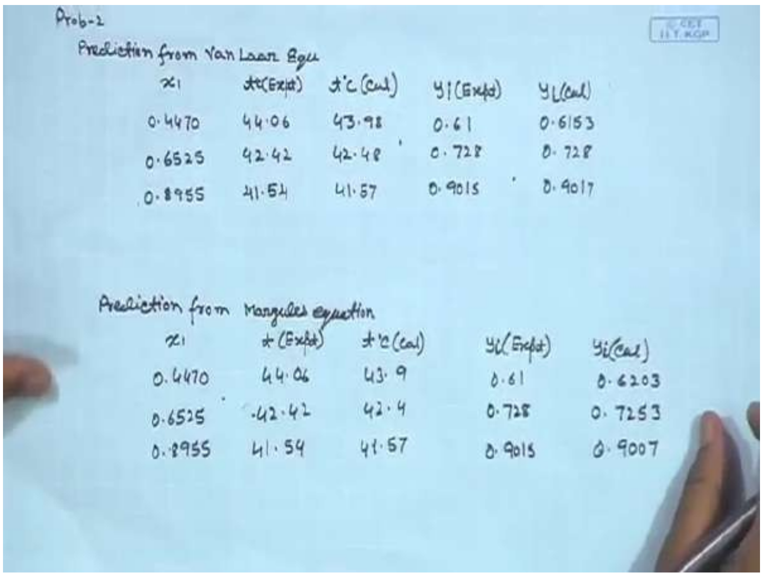

So therefore from here we can find out we can repeat this for different values of for the different x1 values which are given and after repeating we find that the calculated t degree centigrade are this and the corresponding y1 values are this. And you can you can compare them and you find that there is although small there is a mismatch between the calculated and experimental values. Now this was when we were using the van laar equation.

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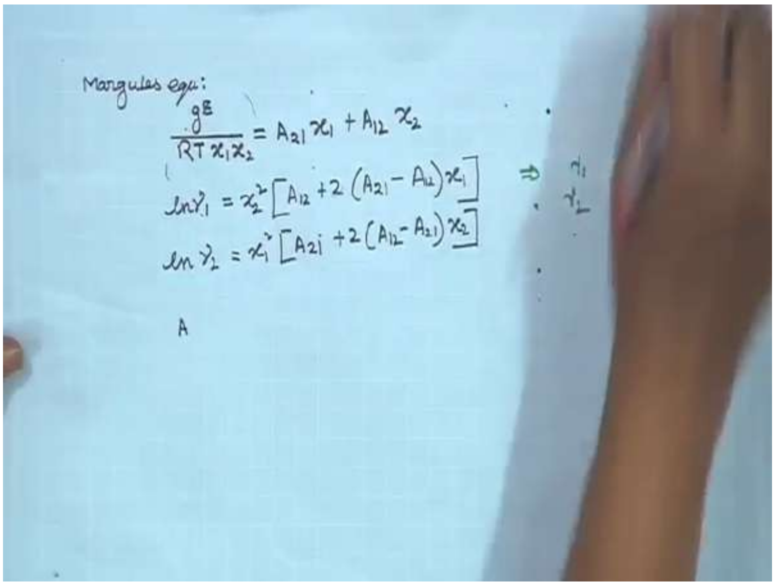

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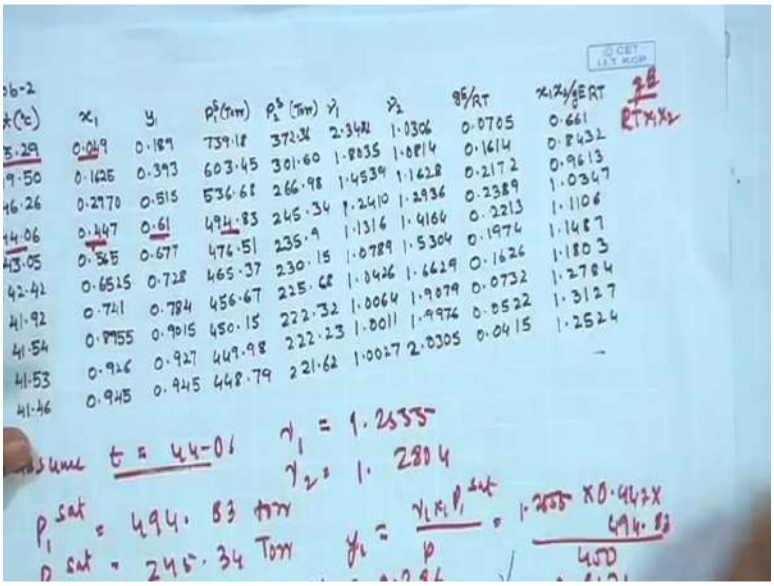

Suppose we would like to do for the 3 suffix Margules equation. The situation is going to be the same, we are going to in this particular case instead of finding out gE by RT this we will be finding out gE by RT X1 X2 and we will be plotting that, right?

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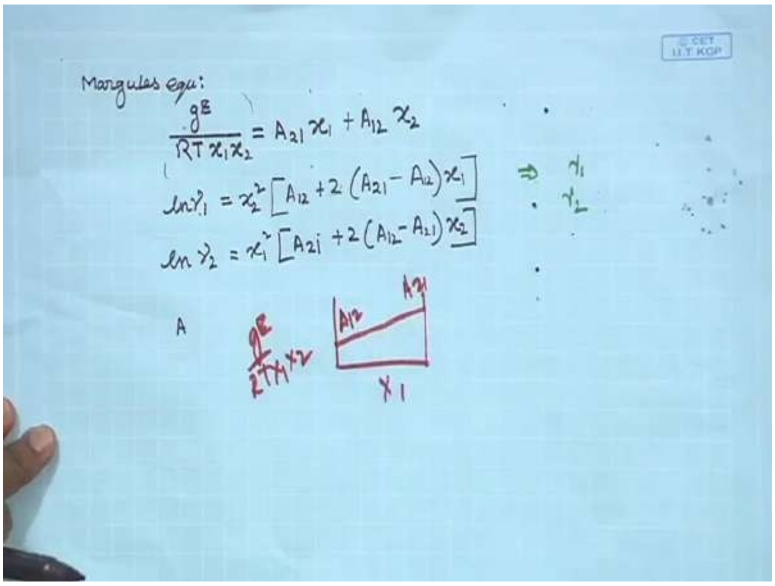

So therefore we can find this out and we can plot it out, if we plot out gE by RT X1X2 as a function of X1 again from the intercepts we know that at X1 equals to 0 we will get A12 here we are going to get A21, right?

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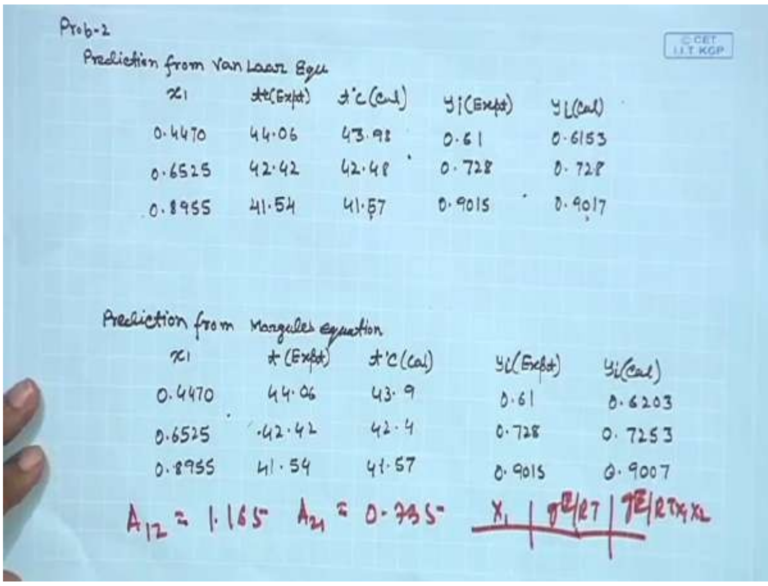

So therefore we can proceed in the similar fashion and we can find out A12 and A21. In this particular case also we find that A12 in this particular case is going to be 1.165 A21 is going to be 0.735 and then once we know this we are we can find out X1 gE by RT as I have mentioned and gE by RT X1 X2 and you can prepare this table.

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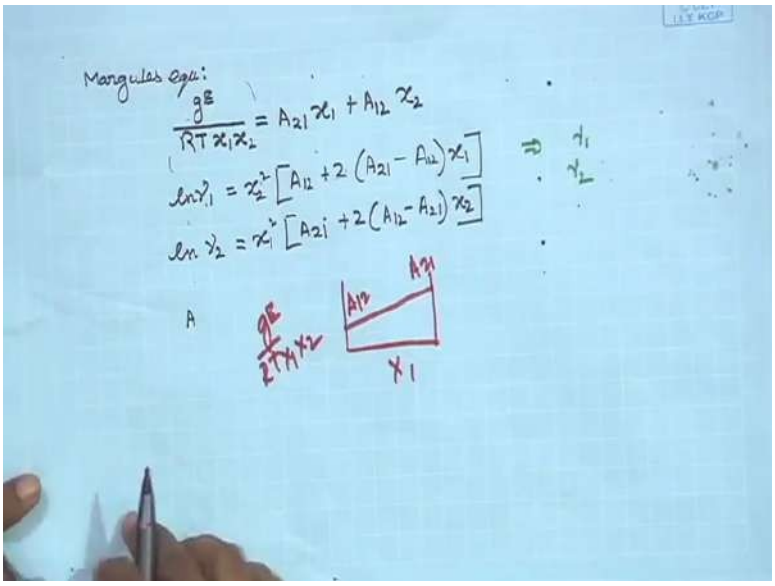

Once you have prepared this table then you can find out ln gamma 1 ln gamma 2 for different x1 x2 values.

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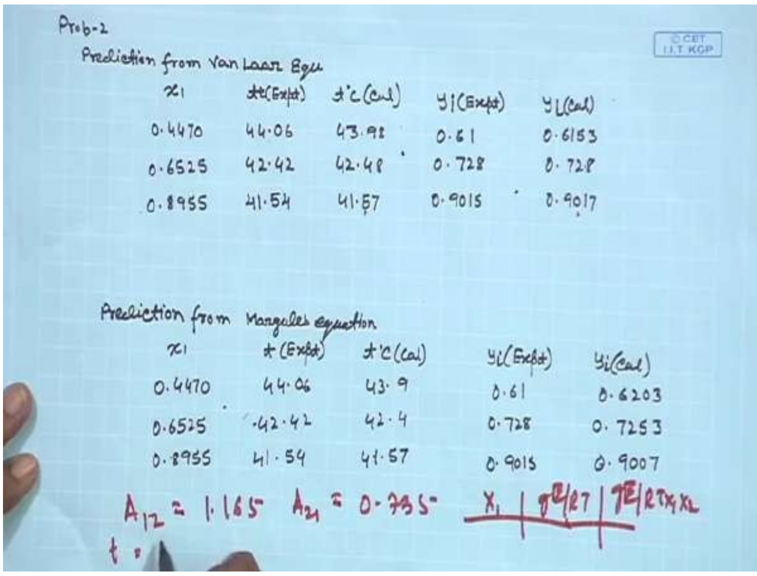

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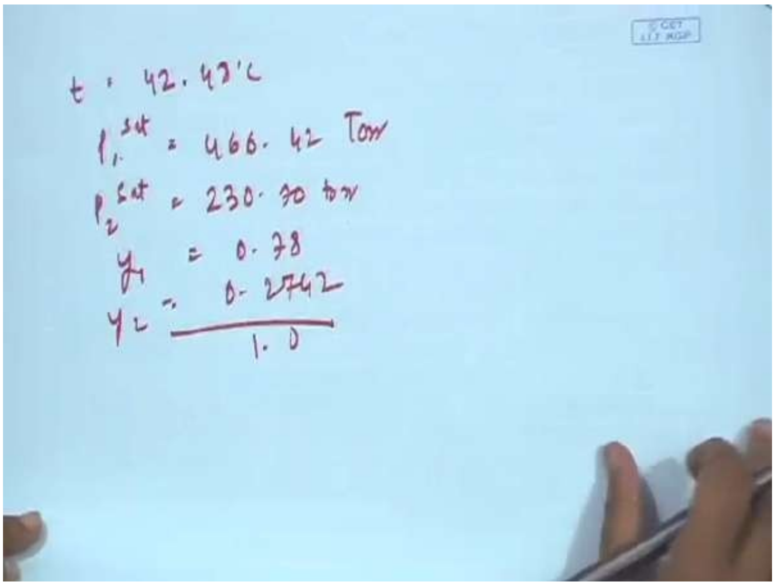

And you can take up or you can assume a value of t, naturally the assumed the value will be closed to the experimental value and for each particular assumed value you can find out y1 y2 and you can find out the summation, see if the summation is close to 1 or not.

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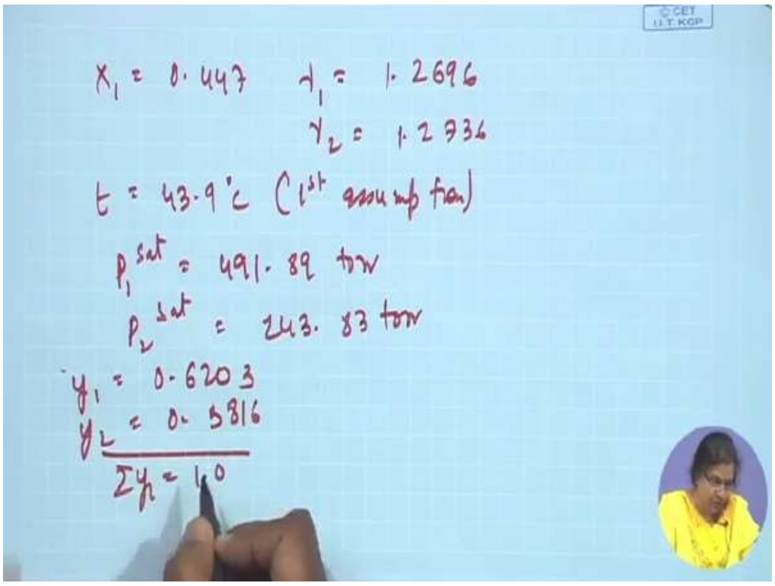

Or else we go for a different sort of an assumption, say for example in this particular case let us take up X1 equals to 0.447 I think have already mentioned gamma1 is 1.2696 gamma 2 is equal to 1.2736 t equals to say at the first assumption, first assumption is the experimental value naturally as I have told you. For this case we have to start from the very beginning from P1 saturated and P2 saturated these are the values that we get from here we get y1 equals to 0.6203 we get y2 equals to 0.3816 more or less we will find that Sigma yi equals to 1.0.

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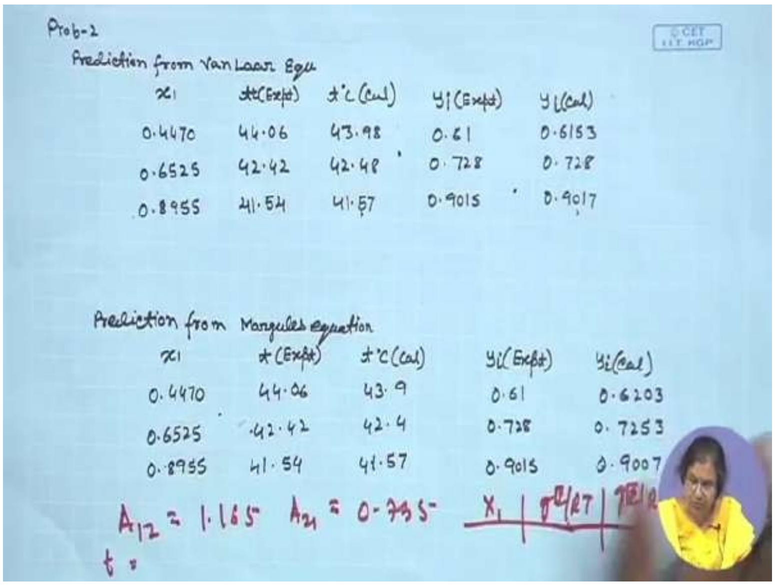

So accordingly we can calculate for the different cases also and we get the yi calculated. Now when we compare the experimental versus the calculated value for both the van laar and the Margules equation in both the problems that we have dealt with we find that the van laar equation appears to be much more accurate in these particular cases.

Well so what did we do? We have been discussing the reduction of isothermal an isobaric data from some fragmentary experimental data if we have that. Now we know that the calculations of gammas and the calculation of the corresponding constants for the excess Gibbs free energy model it becomes much simpler if we know that there is an Azeotrope formation in at any particular position, right?

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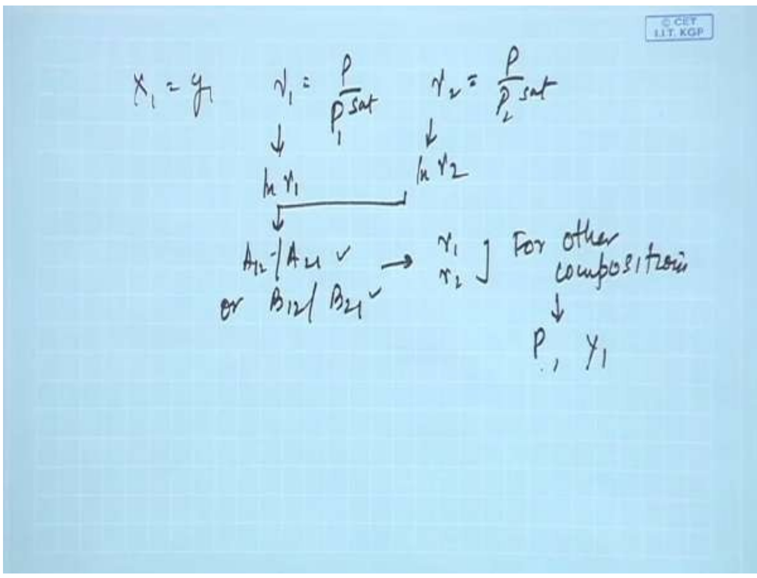

Why does it happen? We have already discussed at the Azeotropic point what happens X1 becomes equal to y1 and naturally under this condition y1 becomes equals to P by P1 saturated, isn't it? So therefore we get y1 equals to P by P1 saturated gamma 2 becomes P by P2 saturated. So therefore it we are finding out of gamma 1 gamma 2 becomes very easy at the Azeotropic point. Once we have found this out we can find out ln gamma 1 ln gamma 2 and then we can select any of the excess Gibbs free energy model it can be van laar or the Margules.

So from here we find out the constants from both these we can find out the constants A12 A21 or B12 B21 as the case may be. Once we know this we can find out gamma 1 gamma 2 for other compositions and once we know that we are in a position to find out P and we are in a position to find out y1.

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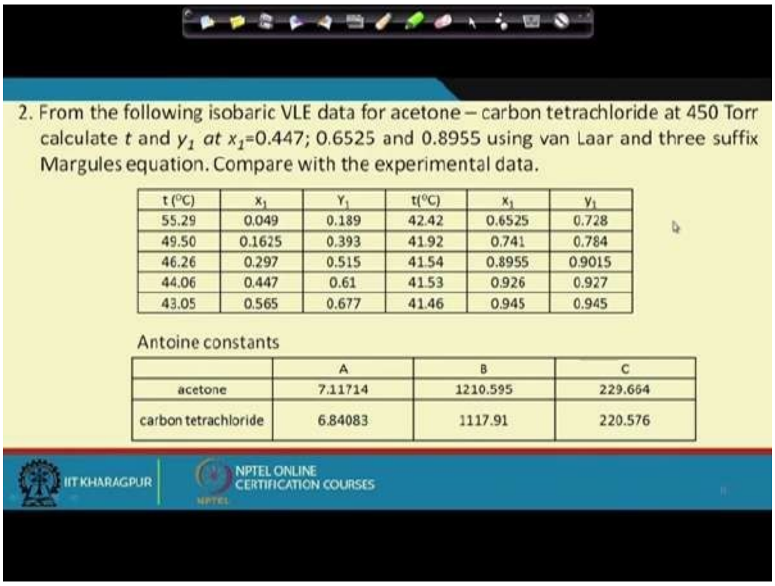

Let us take up a specific problem in order to discuss this Methanol acetone we know that it that it forms an Azeotrope at 760Torr with x1 equals to 0.2 and t equals to 55.7 degrees centigrade it's given here. We are required to predict the Pxy data under this condition.

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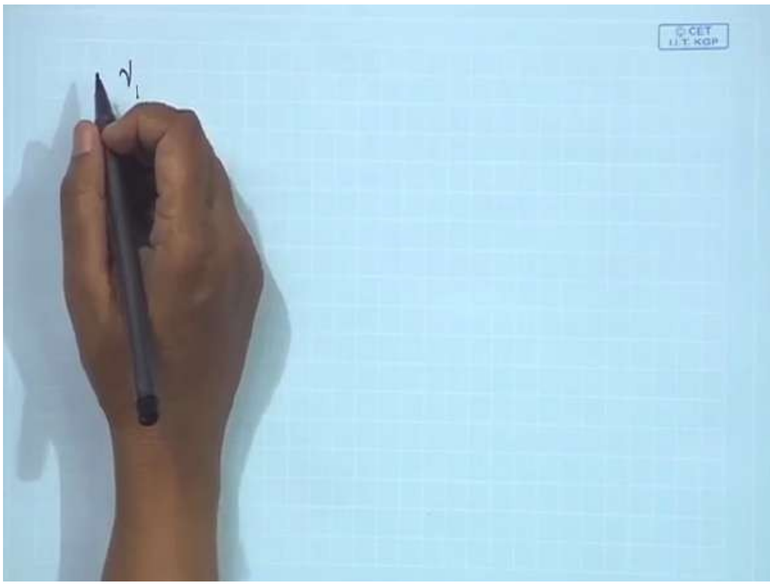

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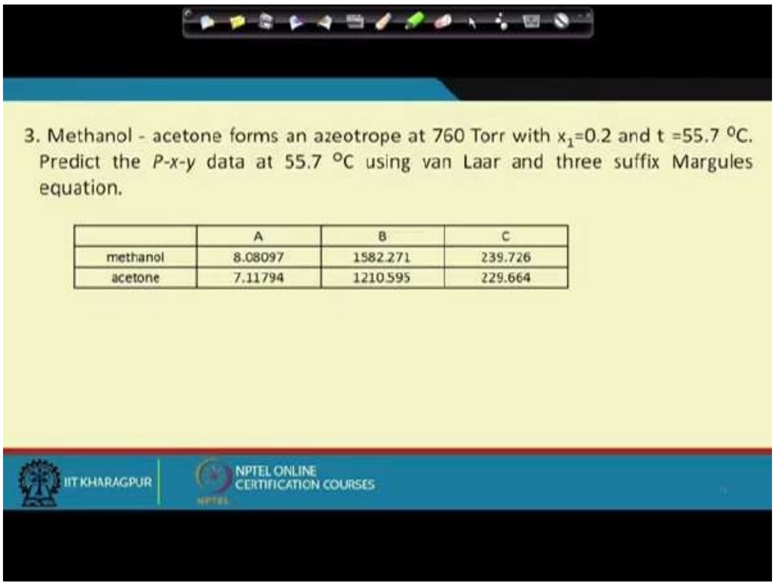

Finding out gamma 1, so therefore what are we supposed to do under this particular condition? We can find out the P1 saturated and P2 saturated and we can find out the gamma 1 and gamma 2 for this particular case isn't it? So therefore at t it's given t equals to 55.7 degrees centigrade, right? For this particular case, what is P saturated for methanol? This is equal to 530.97Torr, P saturated for acetone 749.65Torr, agreed?

What is gamma methanol say? Under this particular condition this becomes 760 by 530.97 1.4313 which gives ln gamma methanol as 0.3607. Similarly for the acetone case we get this as 760 by 749.65 which gives us 1.0138 which gives us ln gamma acetone as 0.0137.

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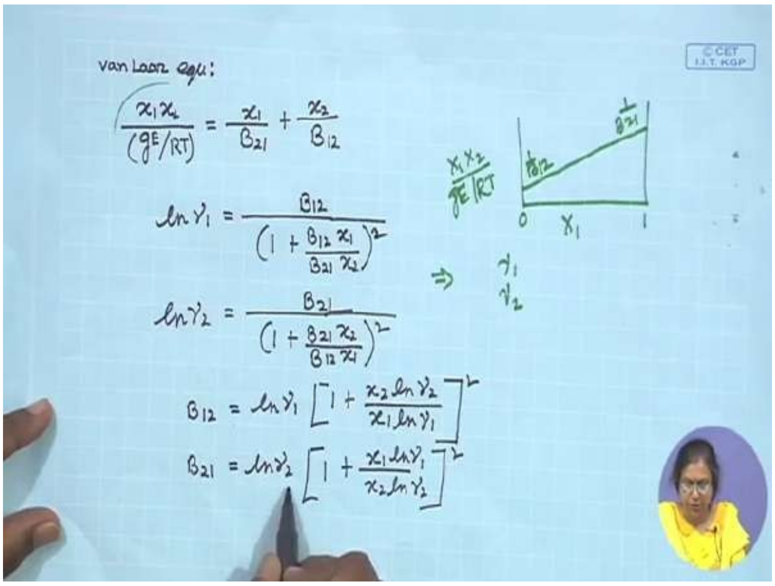

Now we can either take up the van laar equation or the Margules equation. The matter whatever we take up, if we take up van laar equation we can find out B12 and B21 we know gamma 1 we know x2 x1 at the Azeotropic point. So for the Azeotropic point we were in a position to find out B12 and B21 once we can find out B12 and B21 at the Azeotropic point we know that it does not vary with composition. So therefore we can find out ln gamma1 ln gamma 2 for other x1 x2 values as well and then from there we can generate it, right?

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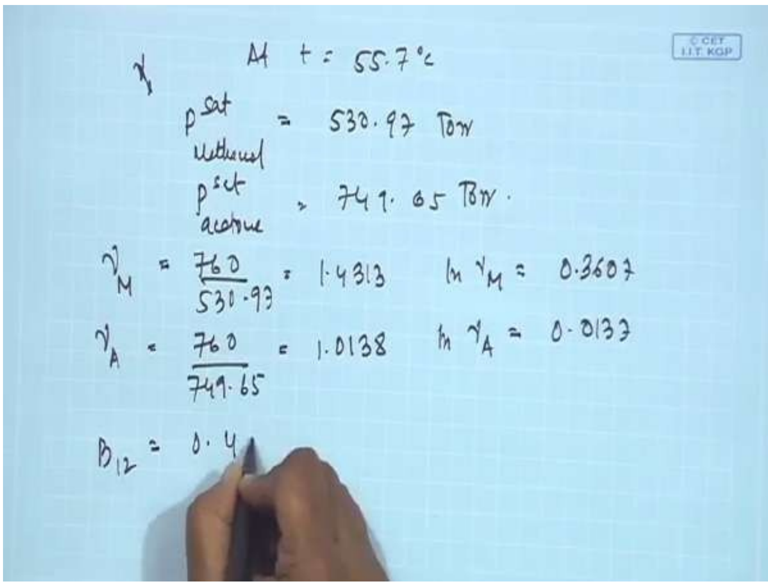

So in this particular case we find our B12is 0.4786 B21 was 0.7878 so therefore we have found out everything for the Azeotropic point.

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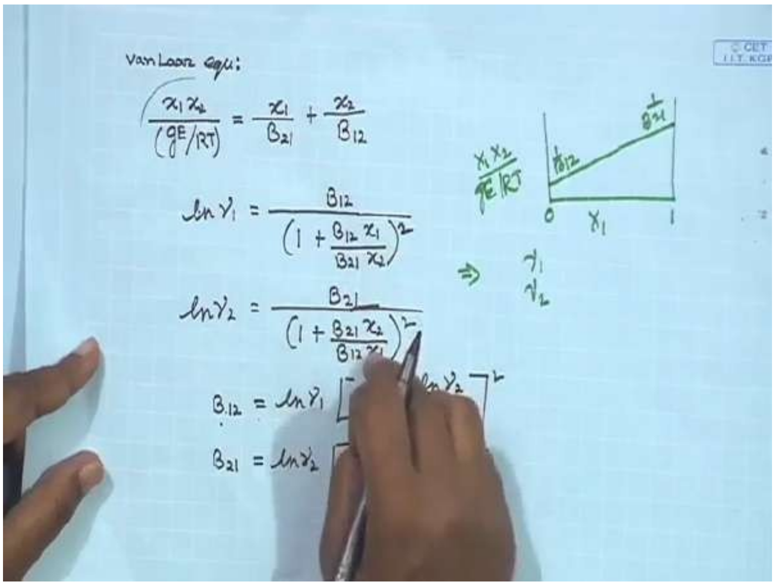

Now let us go to some other composition say at X1 equals to 0.1 from this we can find out gamma1 I have already shown you the equations from where you are supposed to find out gamma1 and gamma 2.

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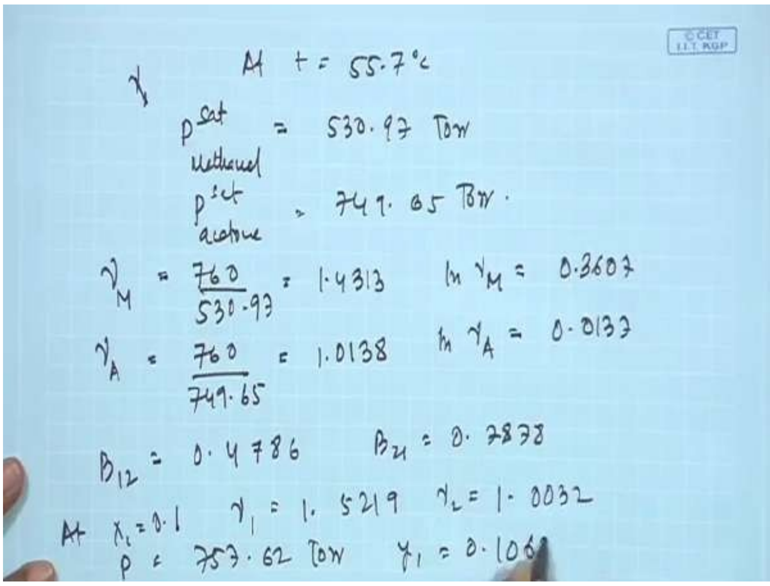

So therefore in this case we find gamma 1 equals to 1.5219, gamma 2 is 1.0032, so P in this case 757.62Torr, y1 comes to as 0.1067, right?

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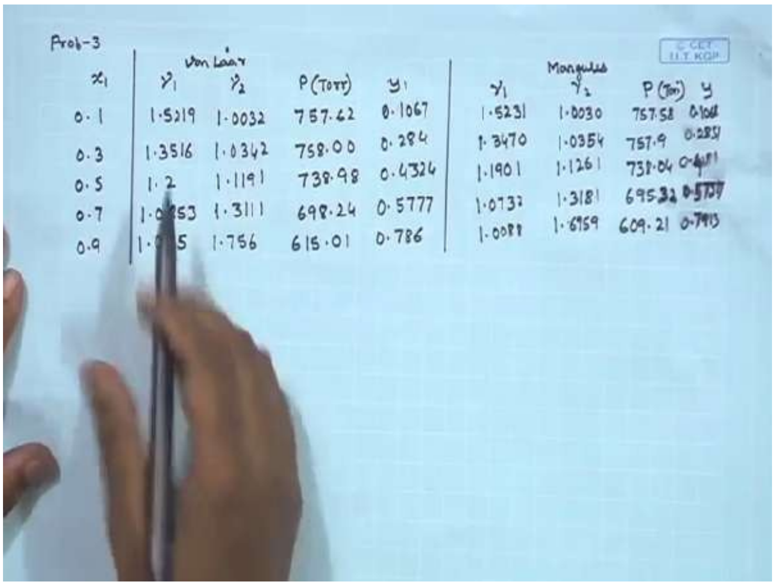

Now in the in a similar way you we can find out the gamma1 gamma2 P and y1. For other composition in the liquid phase and this in this way we can generate the Pxy data for using the van laar equation in much more simpler fashion provided we know that there was an Azeotrope at a specific condition of x1 equals to 0.2. Same thing can be repeated for the Margules equation as well.

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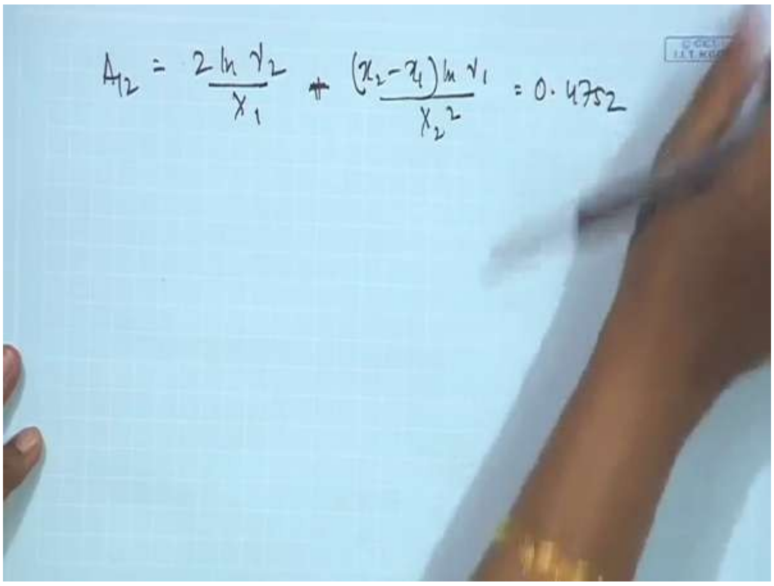

For the Margules equation also we can find out A12 and A21, how to do it? What is A12? 2 ln if you reduce the equation you find that this is going to be 2 ln gamma2 plus x2 minus x1 ln gamma1 by x2 square this becomes 0.4752. Similar way we can find out A21 just in the similar way 2 ln gamma1 by x2 minus x1 minus x2 ln gamma2 by x1 square this become 0.69.

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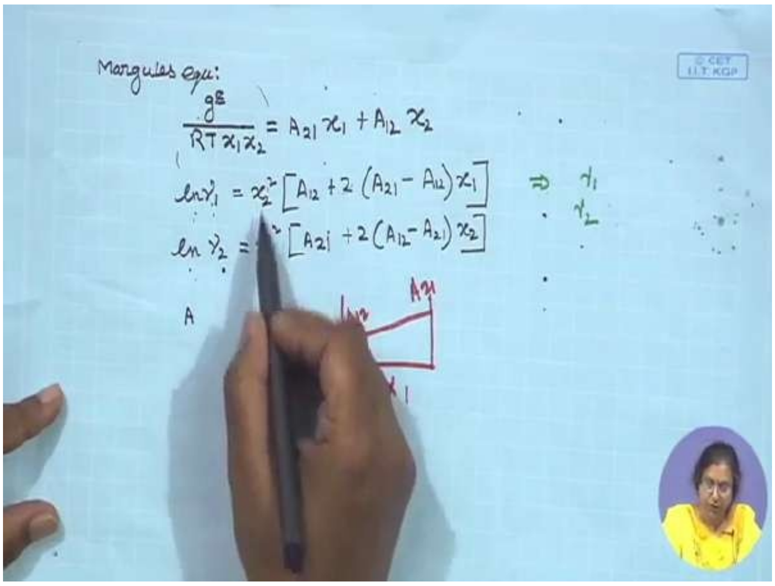

Once we know these 2 then naturally we know A12 below A21, we are in a position now to find out ln gamma1 ln gamma2 for different values of x2 and x1.

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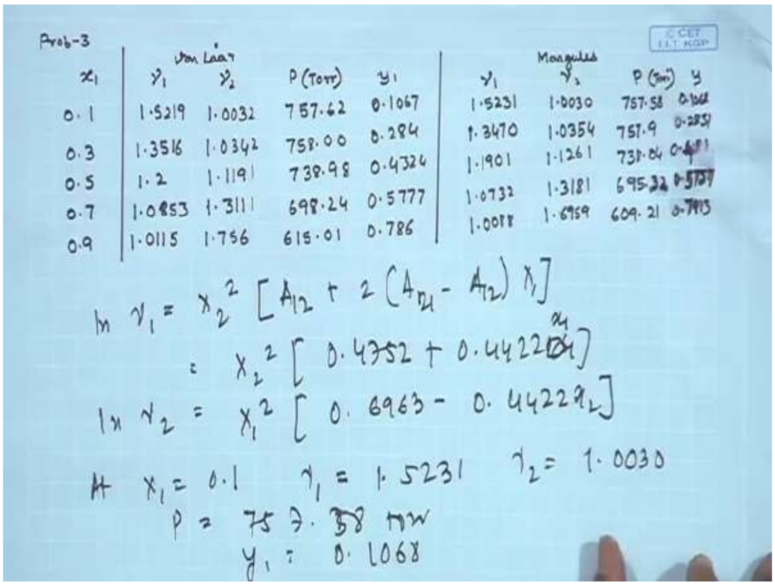

This has been done here, right? So here we have repeated the same thing. For example suppose we want find out ln gamma 1 its X2 square you can just compare since it is A12 plus 2 into A21 minus A12 into x1 this reduces to X2 square 0.4752 plus 0.4422 x1, right?

Same way can find out ln gamma 2 it will be X1 square into 0.6963 minus 0.4422x2, right? So we can find this out.

Once we know this then at say X1 equals to 0.1 gamma1 this becomes 1.5231 gamma2 becomes 1.0030 P you can calculate 757.58torr y1 it becomes 0.1068, right? In the similar way you can calculate it for other values as well for 0.3, 0.5, 0.7, 0.9 and in this way you can generate the entire set of data using 3 suffix Margules equation.

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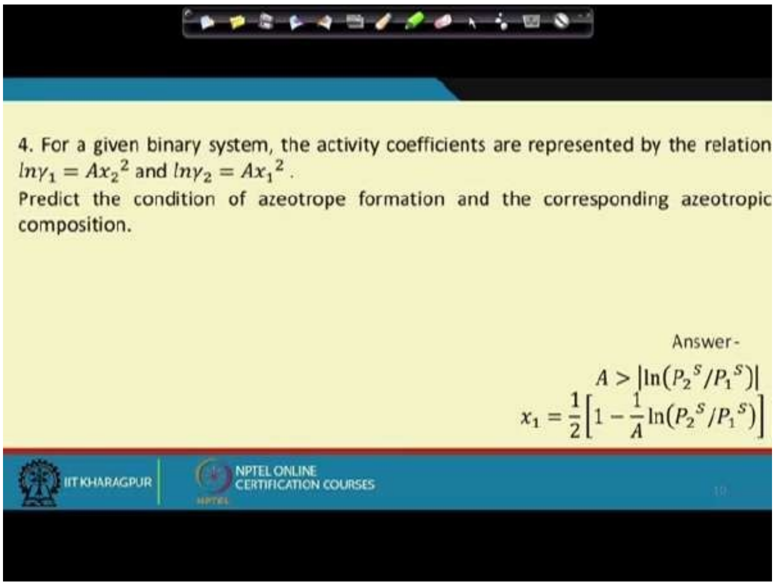

Well, we can take up one more problem as well concerning the Azeotrope, say for instance this particular problem here it is given that for a binary mixture both the components they obey the 2 suffix Margules equation, right?

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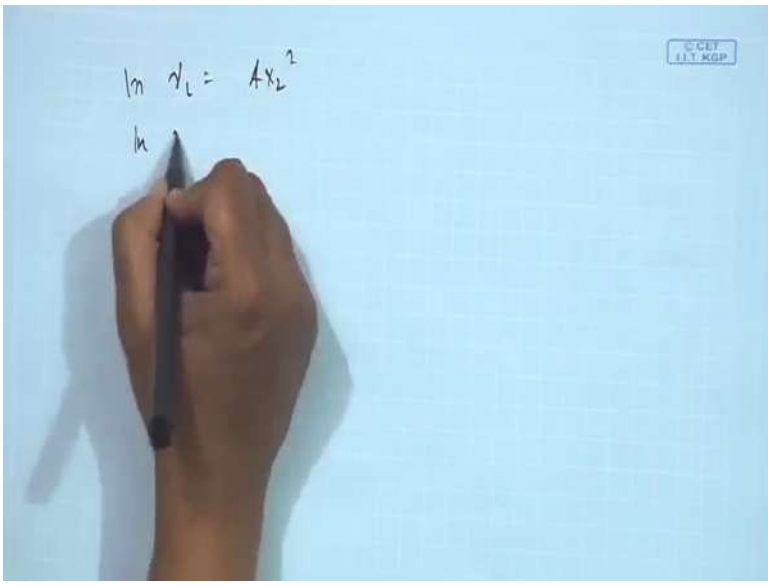

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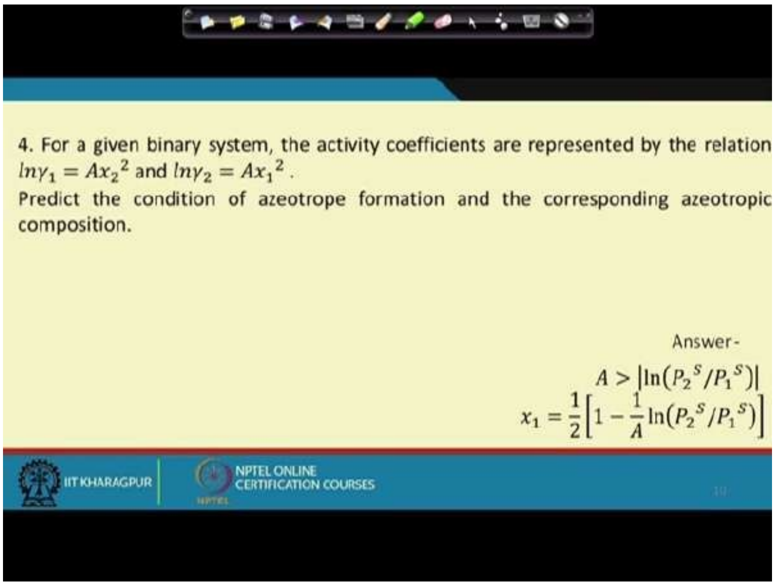

When they obey the 2 suffix Margules equation we know ln gamma 1 equals to AX2 square ln gamma 2 equals to AX1 square and you are required to predict the condition of Azeotrope and the corresponding Azeotropic the condition and the corresponding Azeotropic composition, how to proceed?

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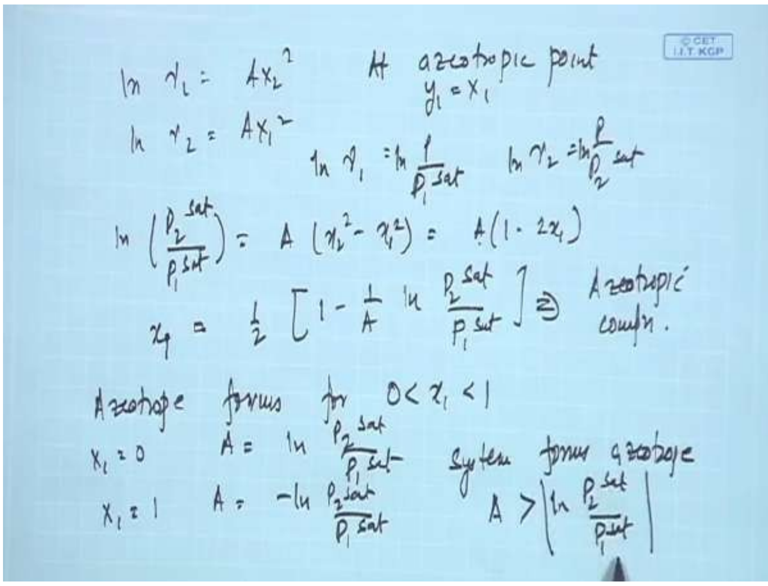

What are the things that you know? You know at the Azeotropic point y1 equals to x1 at Azeotropic point you know it already, right? Accordingly what is gamma 1 you know we just now did P by P1 saturated you know gamma2, P by P2 saturated you know what is ln gamma1 is ln of this; ln gamma 2 is ln of this. Now suppose you subtract one from the other what will you get? You will get ln P2 saturated by P1 saturated is nothing but A into x2 square minus x1 square, isn’t it?

And this is nothing but equals to A into 1 minus 2x1, agreed? So therefore we find that the condition of the Azeotrope should be related to this particular condition and where does the and from this particular condition you know that A into 1 minus 2x1 equals to this. So from there you can find out x1 this is nothing but half into 1 minus 1 by A ln P2 saturated by P1 saturated. So this is the corresponding composition where the Azeotrope forms, this is the liquid phase composition of component 1 where Azeotrope forms.

Now under what condition does it form? We know that the Azeotrope has to form between 0 and between the composition of X1 lying between 0 and 1. So therefore Azeotrope forms for 0 less than x1 less than 1, right? So for x1 equals to 0 what do you get? You get x1 equals to 0 this part has to be equal to 0 for x1 equals to 1 you know 2 has to be equal to this particular part. So therefore once you have obtained them you find that for X1 equals to 0 A should be ln P2 saturated by P1 saturated and for X1 equals to 1 A should be minus ln P2 saturated by P1 saturated.

So therefore when does this system form an Azeotrope can you tell me? System forms an Azeotrope between X equals to 0 to 1. So it has to form an Azeotrope when A has to be greater than ln P2 saturated by P1 saturated. Now we have a minus value we have a plus value so it is safest if we can denote it as A has to be greater than the absolute value of ln P2 by P1 saturated for an Azeotrope to be formed.

Well, so there is one other case also where the calculation of gammas or in other words the VLE calculation becomes much simpler. Usually it's quite well practiced for hydrocarbons and this is known as the K factor. We can use the K factor and find out the VLE data for hydrocarbons in quite a simple fashion.

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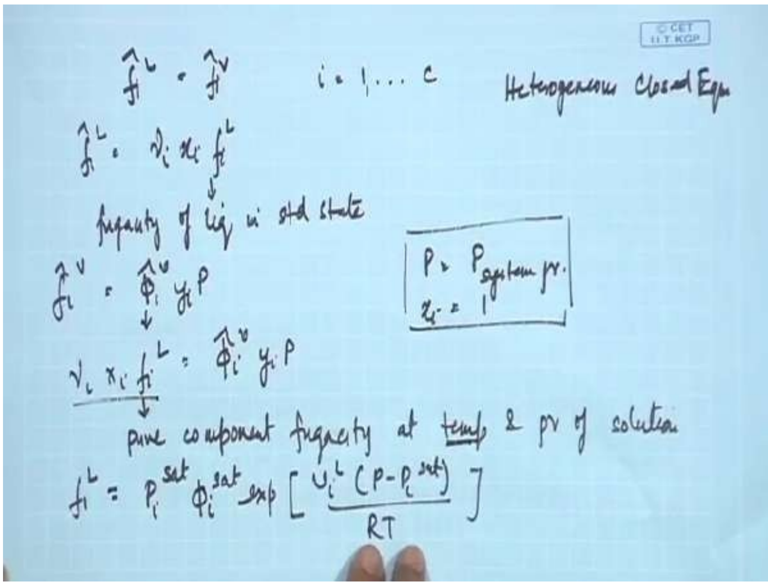

Now what is this K factor? Let us see we find that formation of hydrocarbons usually the intermolecular forces are quite weak. Now since the intermolecular forces are quite weak, so therefore under this particular condition we find that this was the original equation that we had taken. Now when the intermolecular forces are weak, again we can assume the vapor phase to behave as an ideal gas or ideal mixture.

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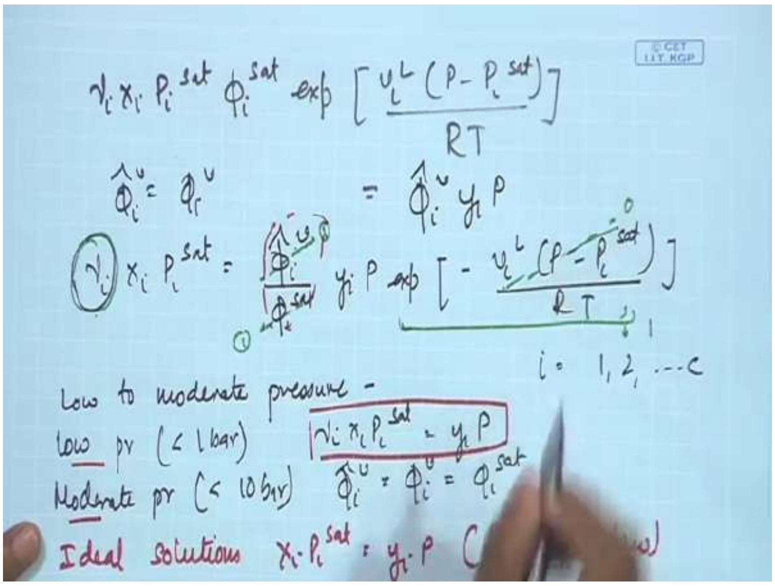

Although it is important to remember that individual gases they do not behave as ideal gases, so naturally for that case what happens? For that particular situation we find that phi i v becomes equals to this particular term this phi i v it is equal to the pure component phi i right and therefore and usually we find that the liquid phase it behaves ideally.

So therefore usually for hydrocarbons we find that this term becomes equal to one this term becomes equal to one this more or less this becomes equal to the pure component vapor phase and this term also it disappears off.

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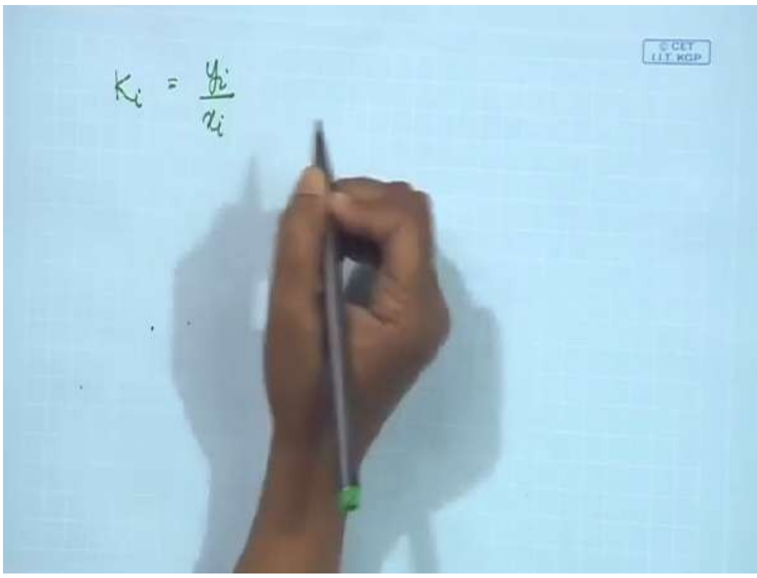

So therefore very frequently what is done is Ki for each particular component the K factor is defined which is nothing but the ratio of the mole fractions in the vapor and the liquid phase.

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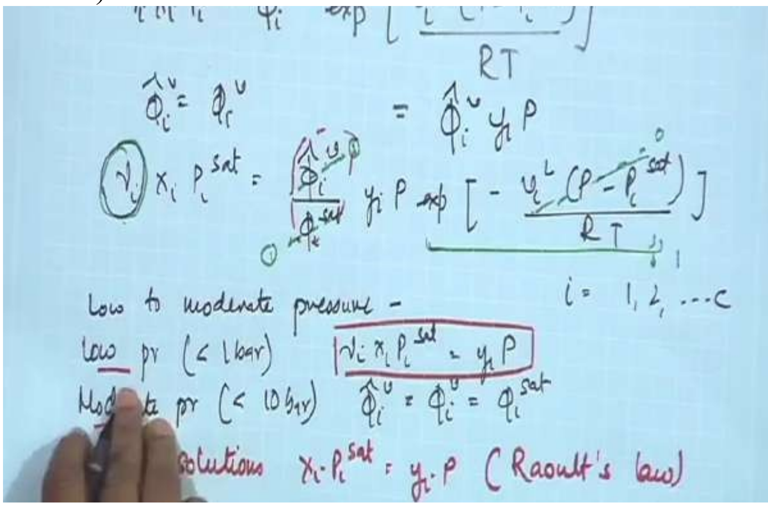
\ 

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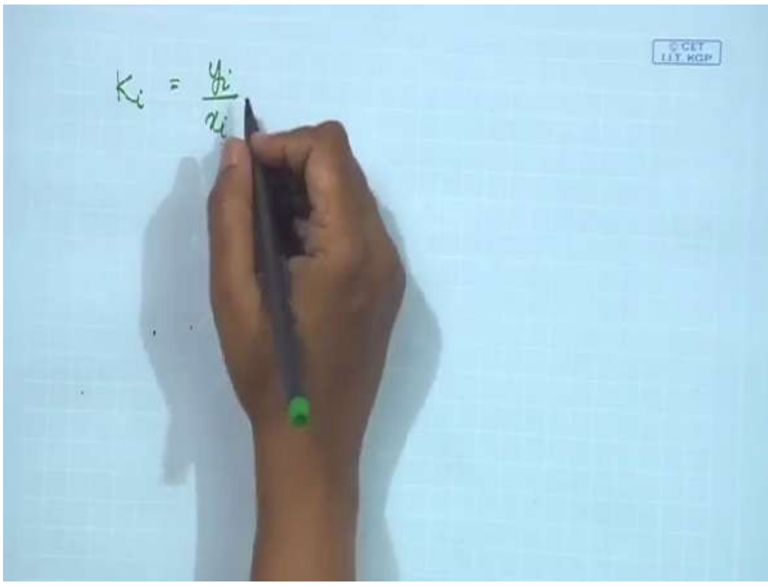

Now from this equation we find what should be the K factor it is gamma i which is usually not there Pi saturated phi i saturated by phi i v into P exponential term definitely remains because the liquid behaves as an ideal mixture but if you're dealing with higher pressures than the poynting correction factor can be found out. So therefore what did we find?

By assuming that phi i v equals to phi i v or in other words the gas mixture behaves as an ideal solution we found out that we are position to find out Ki from all the properties of the pure components of or rather we can find out the Ki from the pure component properties of component i in the vapor phase and in the liquid phase and therefore very frequently what we find? That Kis have been calculated for a large number of hydrocarbon gases and then they are tabulated as functions of T and P.

We find naturally since they are properties of the pure components, they are functions of the pure component properties so therefore they are functions of T and P and lot of effort has been put to plot the K values of individual hydrocarbons as functions of T and P either in the tabular form as monograms.

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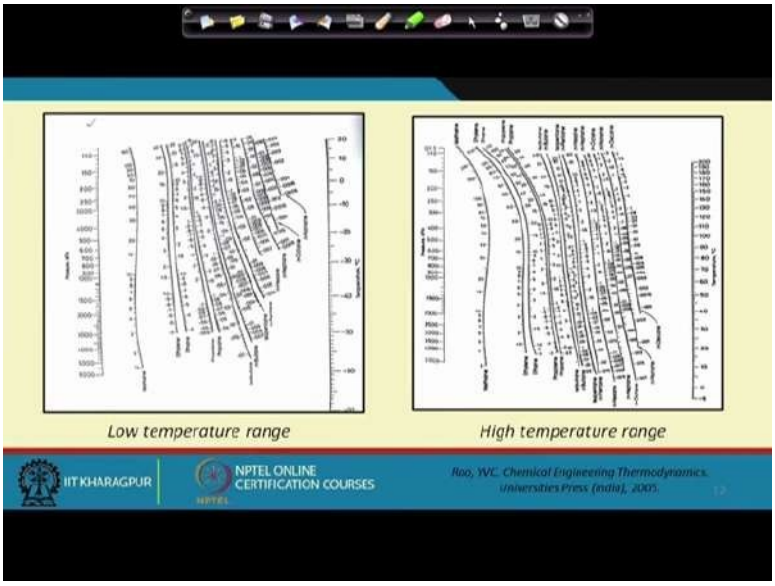

Now the monogram which has been proposed by DePriester and then it has been modified later is as shown in this particular here, here we find that the monograms are presented for the low-temperature range and high-temperature range and these with the help of these monograms where we find that we for each and every hydrocarbon gases if we know the temperature we know the pressure, we are in a position to find out the K values the calculation becomes pretty simple.

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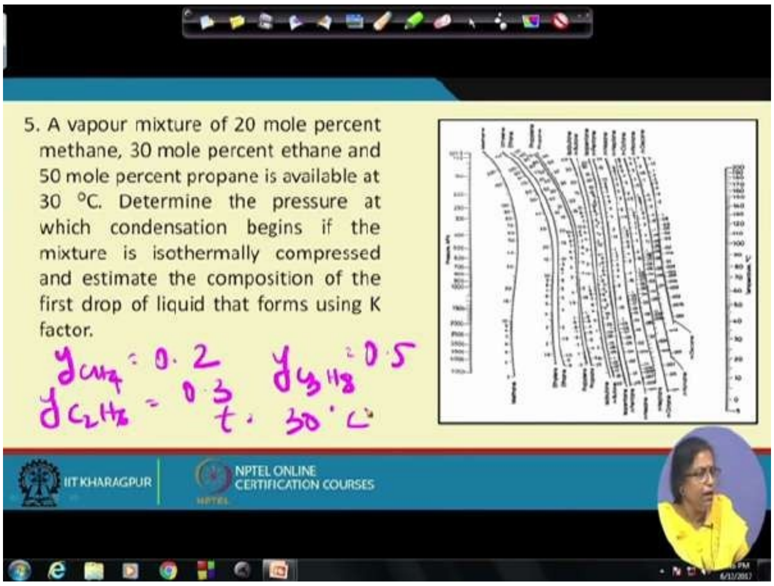

We will just be doing 2 problems and finish off this part. First problem is a vapor mixture, now here it is written that this particular vapor mixture it has y methane it is 0.2 it's written, written that y methane is 0.2, y ethane this is 0.3, y propane it is 0.5, t is given as 30 degrees centigrade, what are you supposed to find? You are supposed to determine the pressure at which condensation begins. How to proceed with this particular case?

Since P is not given you're not in a use this particular K factor chart, you have to guess some particular P.

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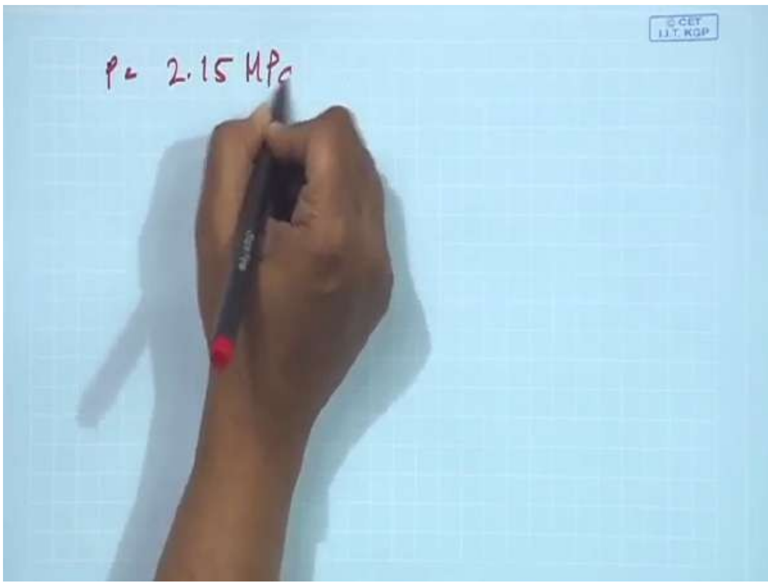

So let us see for the time being let me take the first guess as 2.15MPa.

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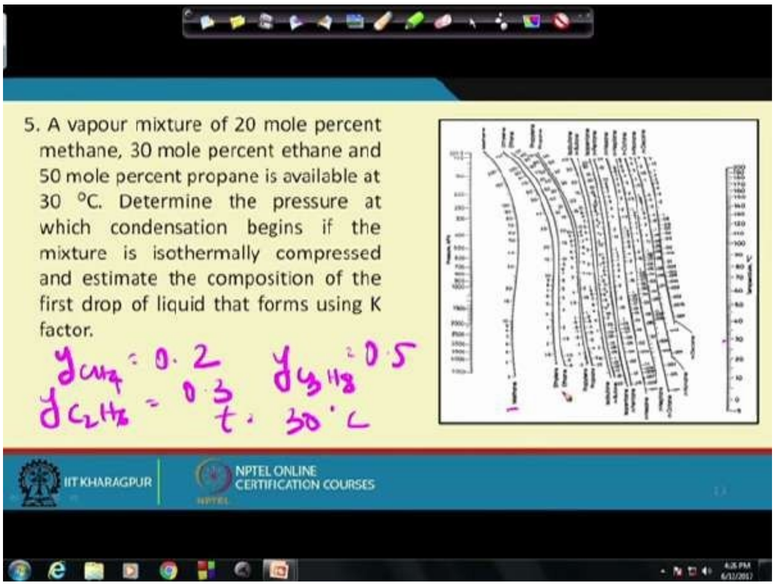

Once I have guess this t equals to 30 degrees centigrade we can draw a straight line from 2.15 megapascal it’s roughly here and it’s about the temperature is 30 degrees centigrade. So if we draw a line we are in a position to find out the y factors for methane, for ethane and for propane.

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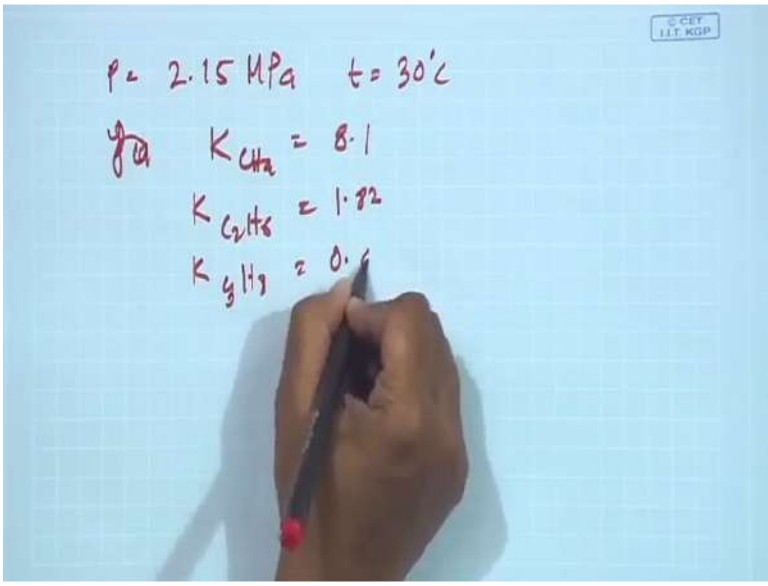

Let us see what are the y factors? We find that for methane the K factor it is 8.1, for ethane it is 1.82 if you draw this straight line you will be able to locate it and for propane it is 0.62. So once you know this once you know the y values it is very easy to find out the corresponding mole fractions in the liquid phase, isn’t it? This comes to 0.0247 this comes to about 0.1648 and for the propane case it's it reduces to 0.8065 if you take the Sigma X1 in this case it’s almost equal to 0.996. So therefore we can say that my assumption of pressure was more or less correct. For greater accuracy you need to alter this slightly and then if you if you get Sigma xi greater than 1 then by linear interpolation you can take the intermediate pressure, okay.

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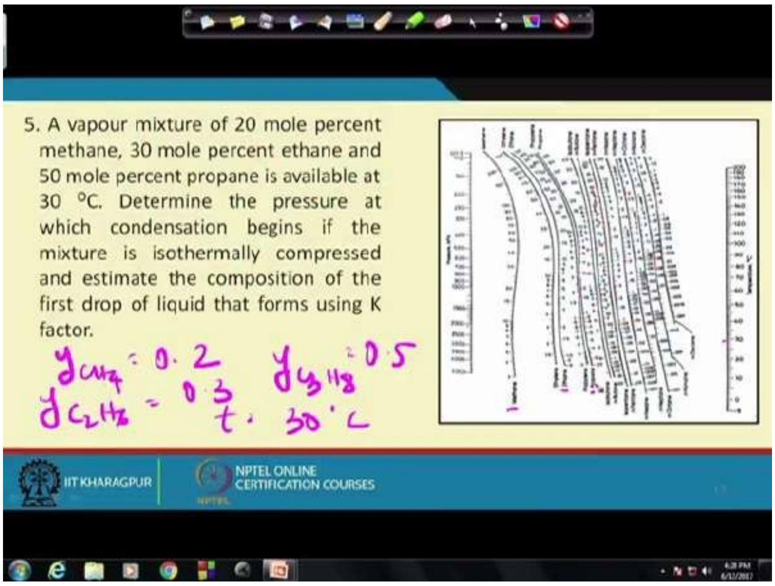

Accordingly you can find out the dew pressure, once you know the dew pressure then with the dew pressure and with the temperature you can find out the K values once more and by using the K values even find out the composition of the first liquid which appears this we had done when the vapor phase composition was given.

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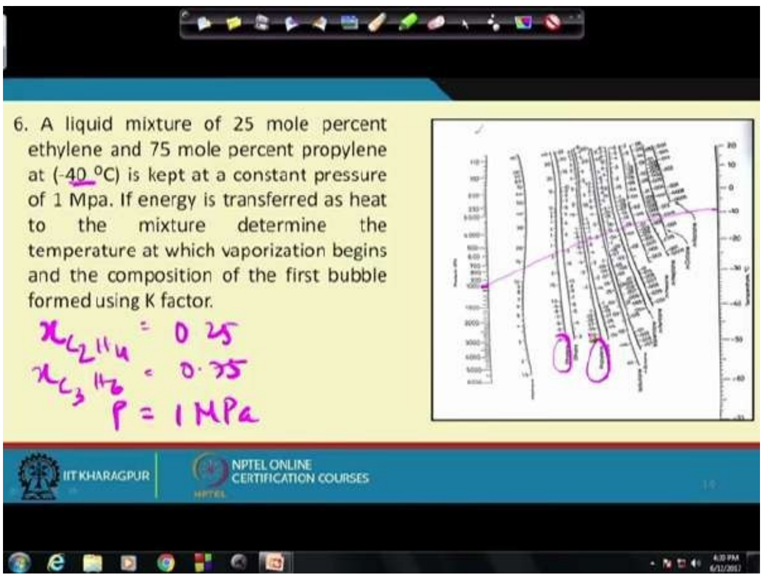

We can also proceed similarly if the liquid phase composition is given as well there is one more problem which we can do in this particular case we find that x of we find that in this particular case x ethylene is provided and x propylene is provided it is there, this is C2H4 and C3H6 this is 0.25 we know this is 0.75 we know the initial temperature was minus 40 degree the pressure is given it is 1MPa.

Now we it’s required to find out the temperature at which the first vapor is going to appear again the same thing there we had assumed the pressure here we are going to assume the temperature. Say for the time being we assume some particular temperatures they are close to minus 10 degree centigrade or something maybe minus 8.5 or something, actually minus 8.5 is the correct answer I know.

So you can start with minus 10 degrees centigrade then you can assume minus 6 or 5 and then by linear interpolation you can find out the actual temperature once you know this temperature you know the pressure again you are supposed to draw, it’s not a straight line you are supposed to draw straight line and then you are supposed to find where it cuts the ethylene where it cuts the propylene.

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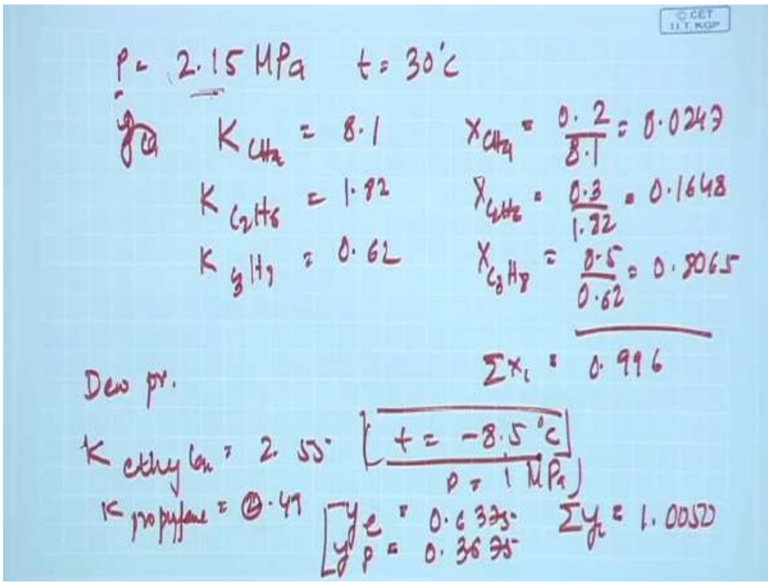

So in this particular case we will find that your K ethylene if you observe, your K ethylene is going to be 2.55 provided I have assumed it as minus 8.5 degrees centigrade P equals to 1Mpa and we find that your K Propylene is going to be 0.49, right? So from there you can find out your y ethylene that is going to be 0.6375 and your y propylene it is going to be about 0.3675 so the sigma yi you’re going to get is 1.0050.

So therefore it can say that the bubble temperature was nothing but equal to minus 8.5 degree centigrade and the corresponding vapor composition can be given by the compositions that we found out.

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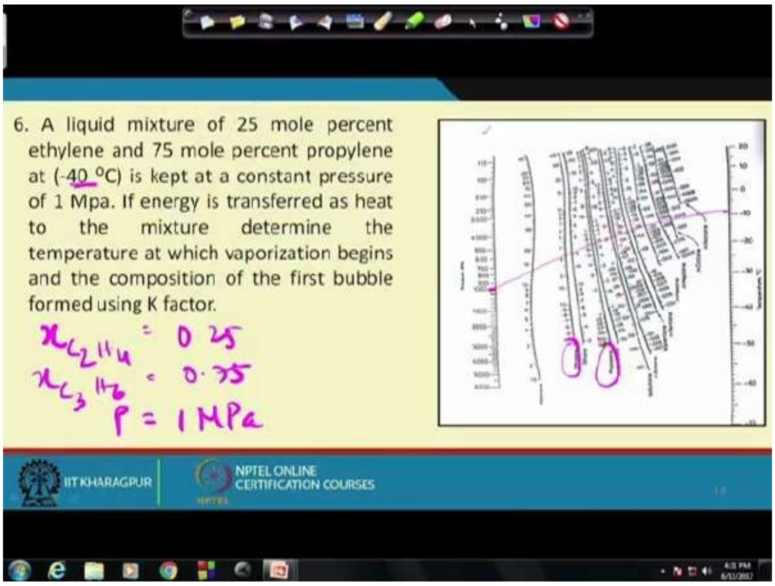

The only thing which we need to do is that we have to start with a guess value; it's not very difficult to guess it properly because it has to lie between the boiling points of the 2 liquids. So we can start with and more or less we know the compositions, so we can start with the weighted mean boiling point and we can go and we can proceed.

So in this particular way what I did was? We discussed different non ideal solutions, the methods of generating the complete Pxy or the Txy date from fragmentary data and how the situation gets simplified when we are dealing with Azeotropic when there is an Azeotrope formation and with the use of K factors, how the situations gets simplified when we are dealing with hydrocarbons mixtures. Now we have been dealing with large amount of rather we have been discussing for quite some time regarding the VLE data of different nonideal solutions.

It is important for us to know that since we are dealing with so much of experimental data whether the data that we have collected or generated is thermodynamically consistent or not whether the data is reliable whether we can proceed with the data. So in the next class we deal with thermodynamic consistency of VLE data before we proceed with any other topic, thank you very much.