Phase Equilibrium Thermodynamics
Tutorial
Module 5
Lecture 32

Good morning everybody my name is Alex Koshy, I am the TA for the course phase equilibrium thermodynamics. So today I will be discussing a few problems that deals with the contents of week 5 of this course there are a couple of problems that deals with the fugacity coefficient estimation and there is one problem after that, that deals with the estimation of molar volume of a mixture from Amagat's law as well as from Dalton's law.

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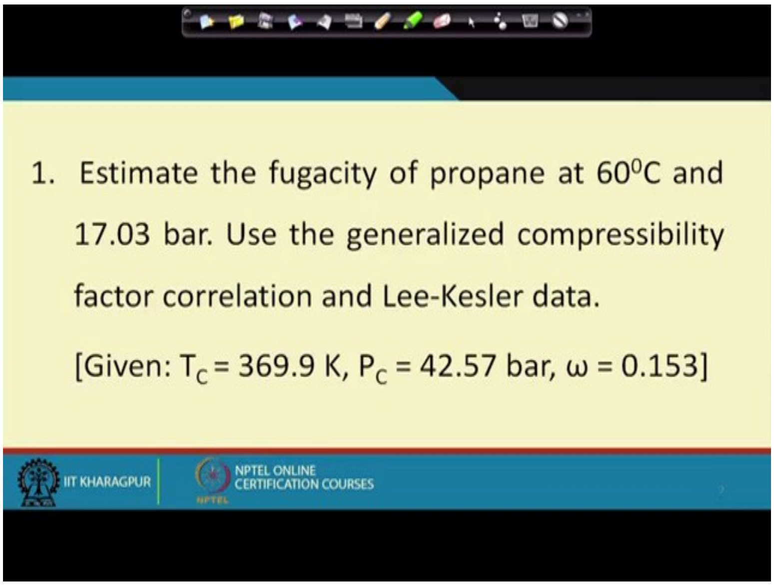

So let me go to the problem first of all. So the first problem I am going to read it out, estimate the fugacity of propane at 60 degree celsius and 17.03 bar. Use the generalized compressibility factor correlation and Lee-Kesler data. So the critical temperature and critical pressure are given Tc is equal to 369.9 kelvin and Pc is equal to 42.57 bar, the acentric factor is given and it is 0.153.

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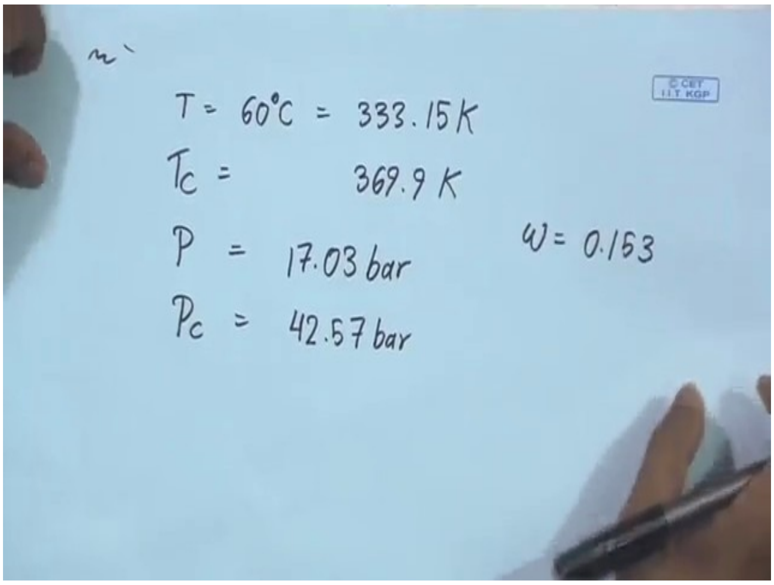

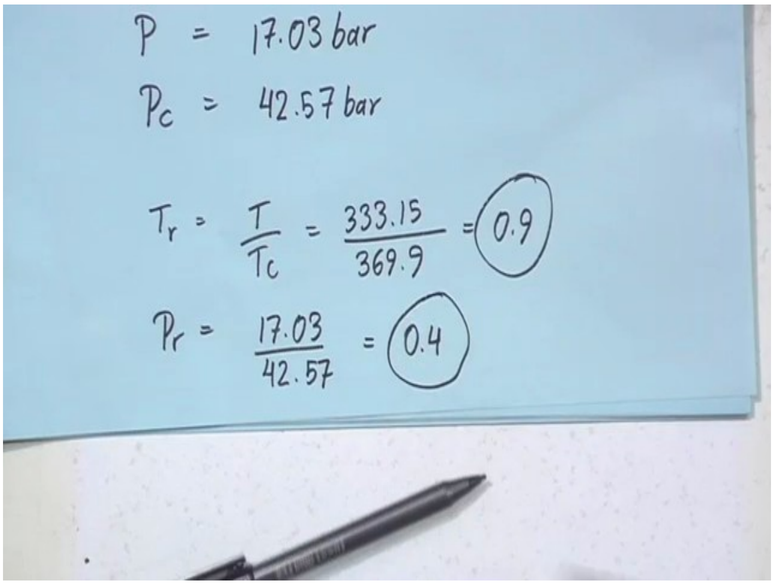

So the first thing that we need to do is we need to list out the values that are given to us. So I am going to do that, T is given, that is 60 degree celsius that is 333.15 kelvin, Tc critical temperature is given and that is 369.9 kelvin, pressure is given and that is 17.03 bar, critical pressure is given 42.57 bar and acentric factor is also given 0.153. So the first thing that we need to find out is, we need to find out the reduced temperature as well as the reduced pressure using these values.

We know the reduced temperature is T by Tc that is 333.15 divided by 369.9 and I have already calculated these values I got the value as 0.9 and then I calculated Pr that is reduced pressure 17.03 divided by 42.57 that is 0.4. So we have the value of Tr, we have the value of Pr.

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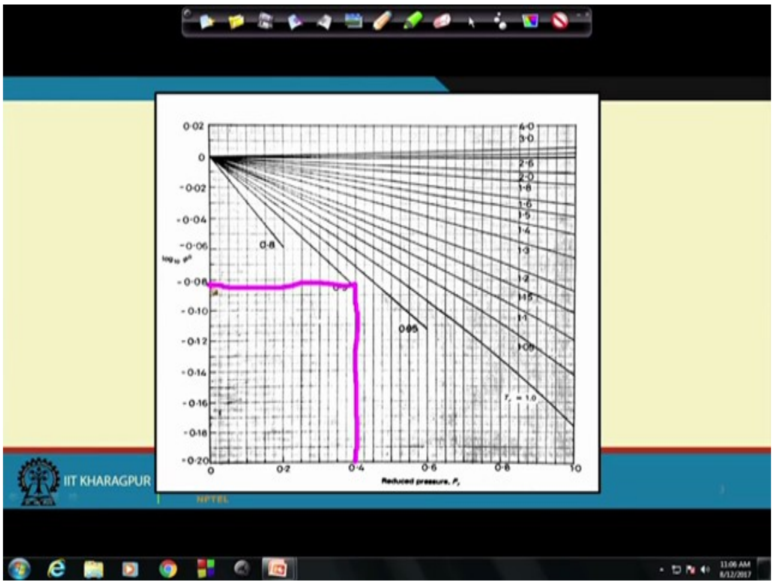

Now from Lee-Kesler chart we need to find out the value of log 10 phi 0, where phi is the fugacity coefficient. So we take this graph here in the x axis reduced pressure is plotted and all these lines corresponds to a different values of reduced temperature. So here we know that our reduced temperature value is 0.9 and reduced pressure value is 0.4, so we start from 0.4. We start going up and when we reaches the reduced temperature line of 0.9 we stop and then we go horizontally to the log phi 0 value.

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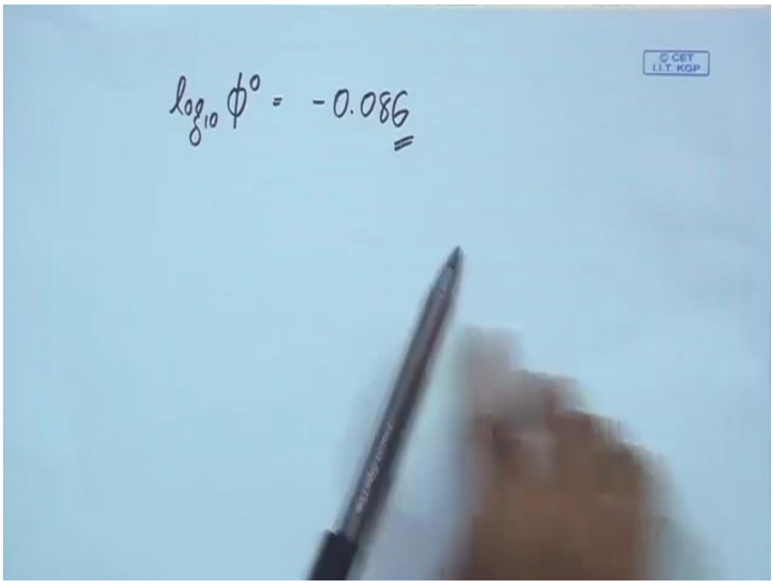

And we got log phi 0 value as minus 0.086. So we keep that value there. Now as we are using a three parameter model we need to find out the log phi 1 value as well.

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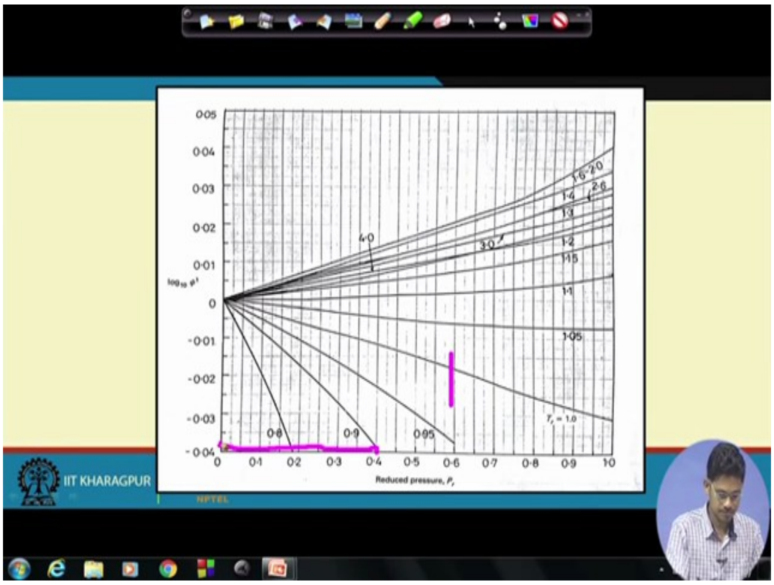

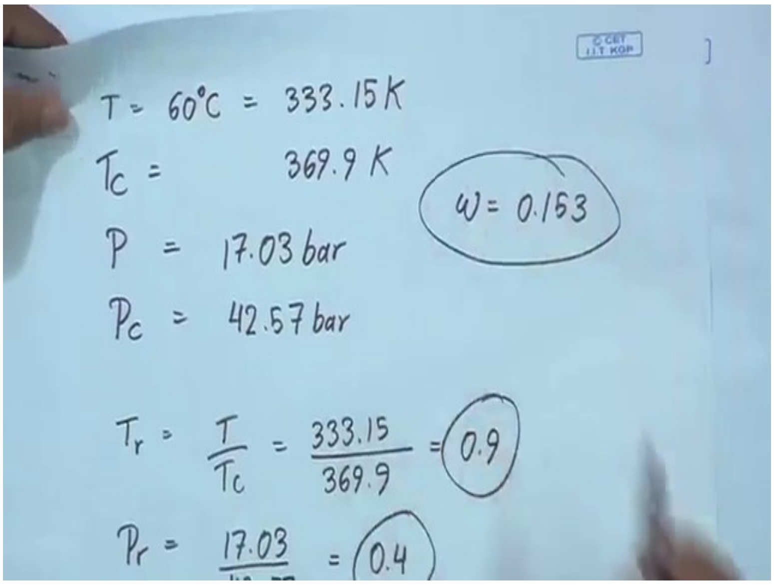

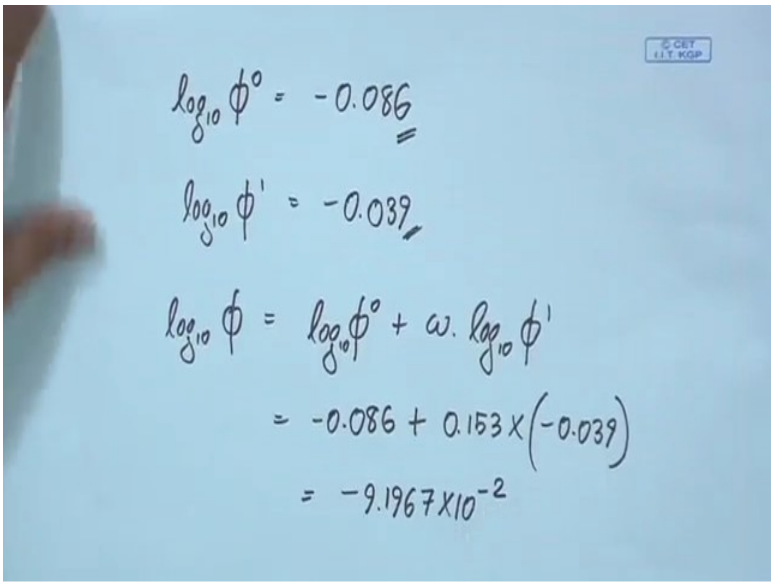

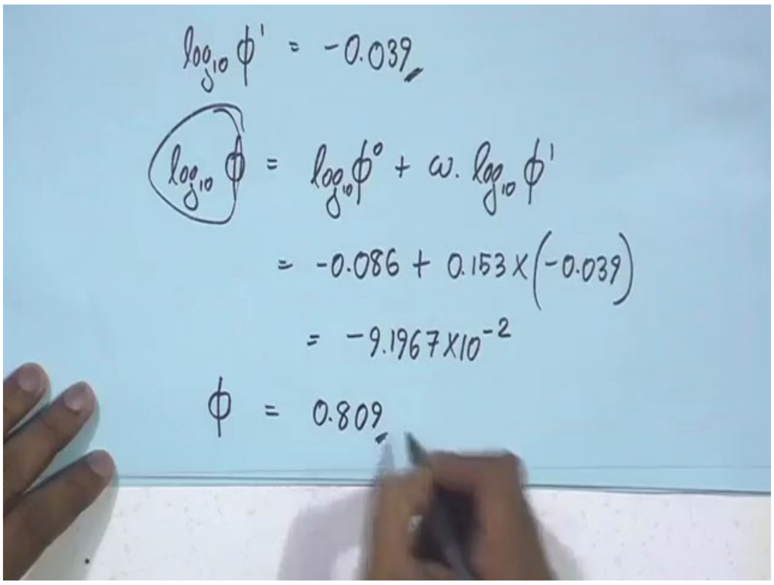

So we go to the next chart. Here we are having reduced pressure 0.4, we go up we reach the reduced temperature line 0.9 and we go horizontally and we get the value of log phi 1 around say (point) negative 0.039, so we got log phi 0 value, we got log phi 1 value. So we need to find log phi value that is log phi 0 plus omega that is acentric factor which is equal to and omega value we already know we have written it down here. So we write that value here, so we get the value of log phi as minus 9.1967 into 10 raised to minus 2.

So we all know how to find out an anti-log of a value using a calculator, so we find the anti-log of this value and we get the value of phi as 0.809.

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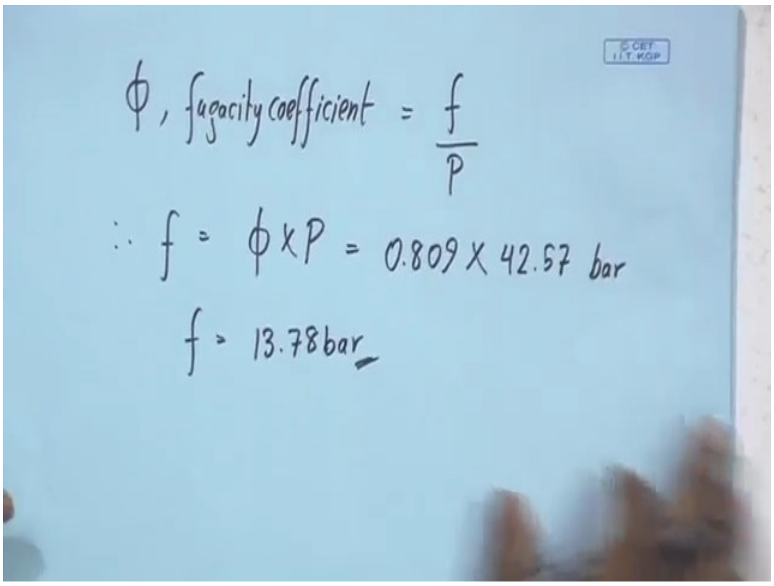

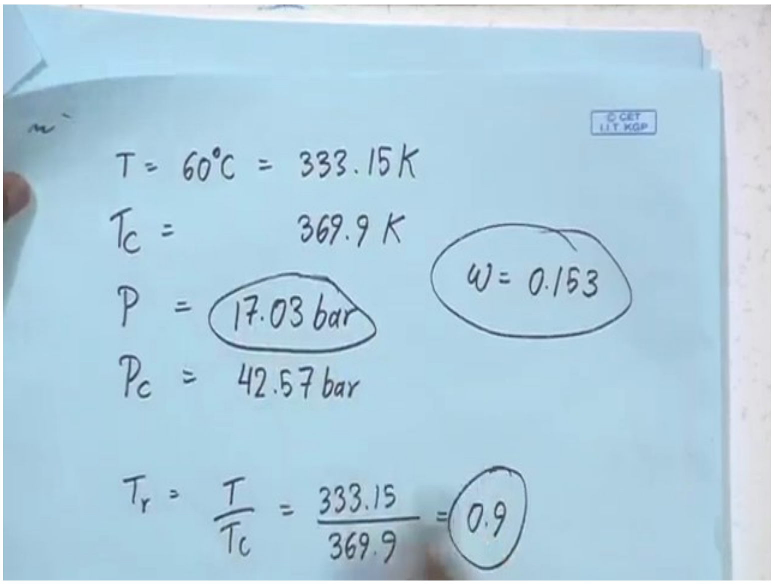

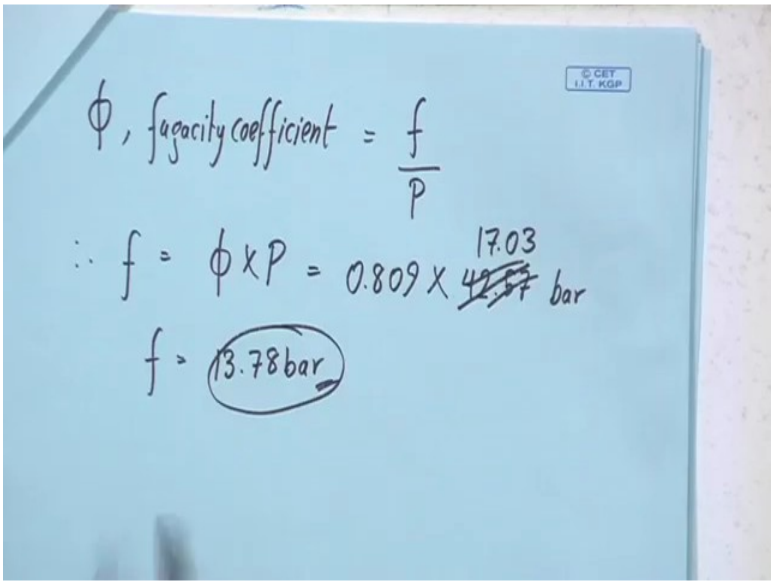

Now we know phi that is the fugacity coefficient is nothing but the ratio of f that is fugacity by pressure. Therefore fugacity that we need to be we need to estimate fugacity is equal to phi into pressure. We know the value of phi 0.809 and we know the value of pressure that is given earlier 42.57 bar. So solving this we get the value of fugacity f as 13.78 bar, alright. I am sorry about this value this is critical pressure. So the pressure that is given the pressure of the system is 17.03 bar so we substitute it here 17.03 phi into P that we get as 13.78 bar, okay.

So what have we done here in this problem we first of all listed out the values that we have we listed out temperature, we listed out pressure, we know the values of critical temperature and critical pressure from these values we found out the reduced temperature as well as the reduced pressure and from the values of reduced temperature and reduced pressure we found out log phi 1 and log phi 0 and from these values using the acentric factor value we found out log phi and from the value of log phi we take the anti-log and we found out the value of phi and from the value of phi we just found out the value fugacity by multiplying phi with the pressure.

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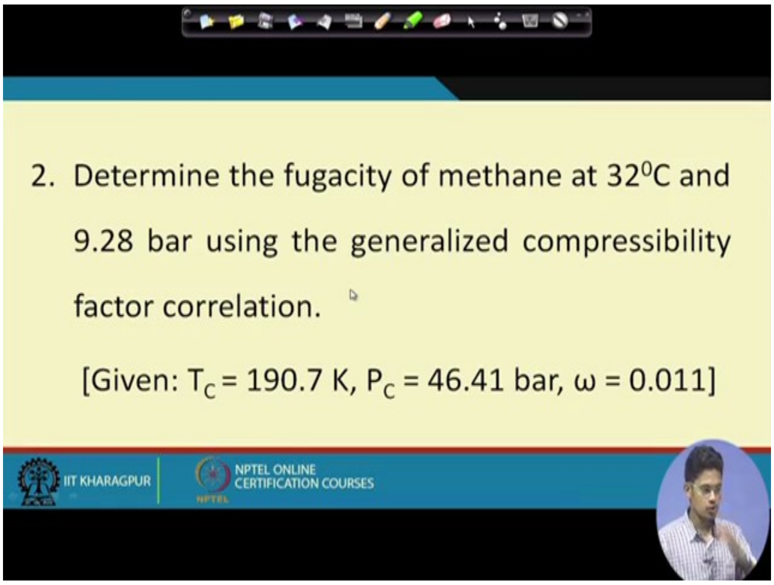

So I am going to do a similar problem that is our second problem, I am going to read out the problem determine the fugacity of methane at 32 degree celsius and 9.28 bar using the generalized compressibility factor correlation. The Tc, Pc and acentric factor values are given. So we proceed in the same way we did in the last problem.

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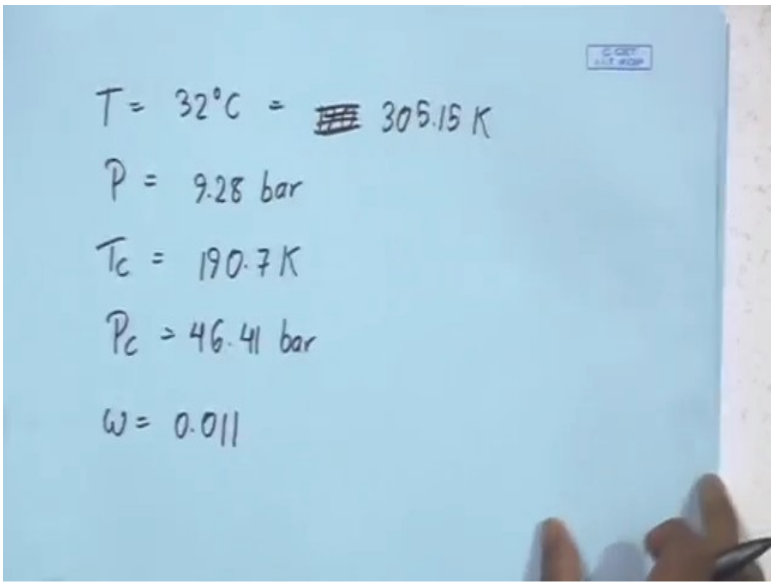

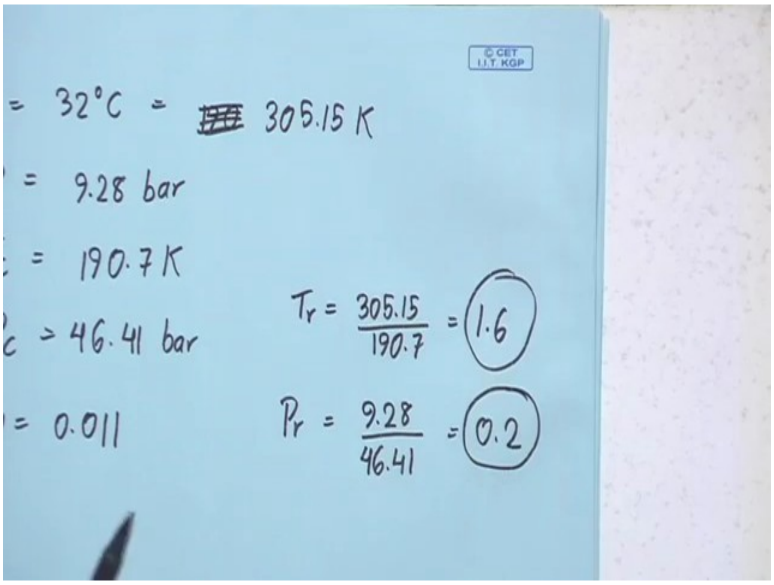

First thing we write down the values T is equal to 32 degree Celsius that is (190) I am sorry that is 305.15 Kelvin, P 9.28 bar, Tc 190.7 Kelvin, Pc 46.41 bar and the acentric factor 0.011, okay. Now we calculate the reduced temperature and reduced pressure values, reduced temperature value we got it as 1.6, reduced pressure value we got it as 0.2. Now we have the reduced temperature value, we have the reduced pressure value so we go to the chart.

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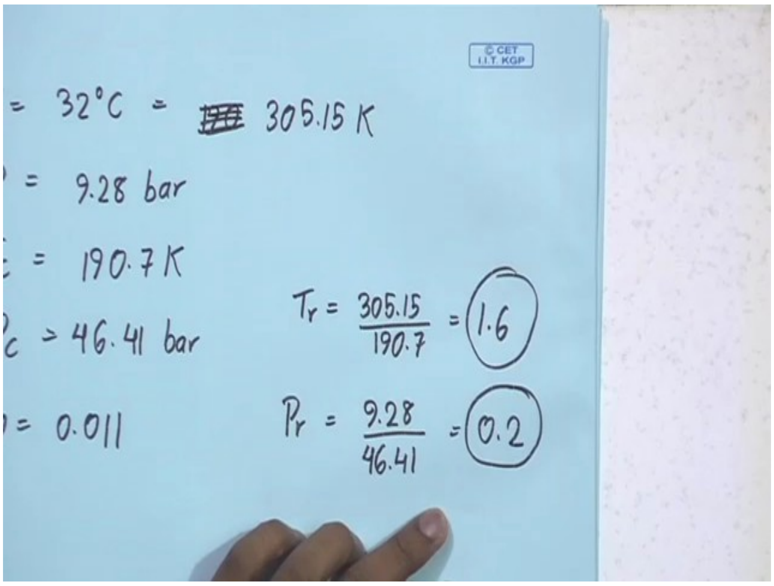

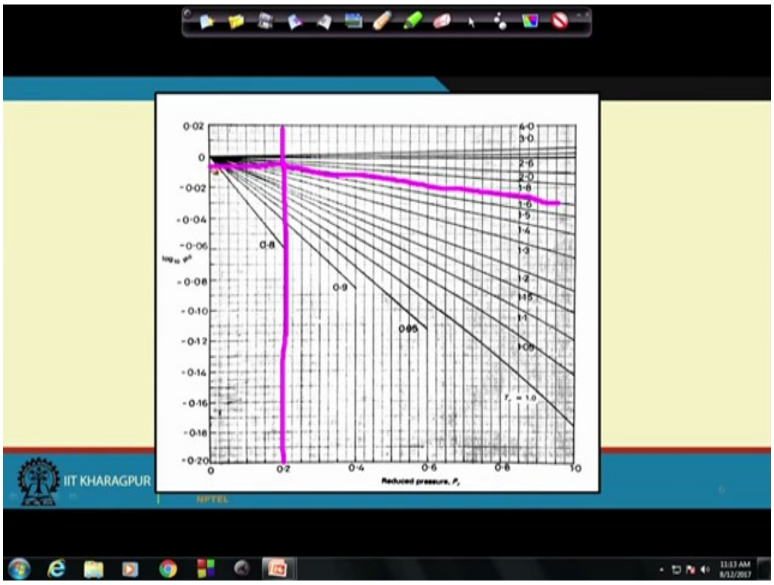

We proceed from reduced pressure value that is (1 point) I am sorry 0.2 we go up. Now we go up. Now we know that the value of reduced temperature is 1.6, so we need to find out the line for 1.6 here it is this line, so it meets somewhere here then we go horizontally to left.

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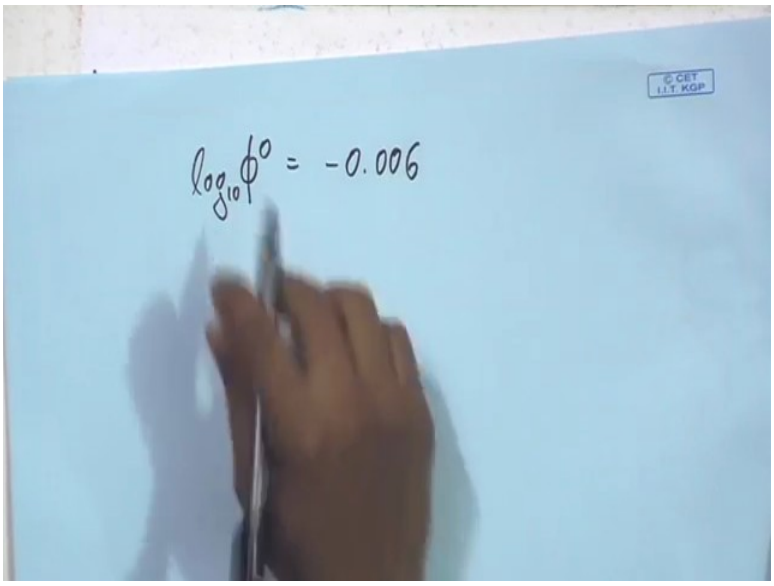

So we get the value of log phi 0 we get the value of log phi 0 as minus 0.006.

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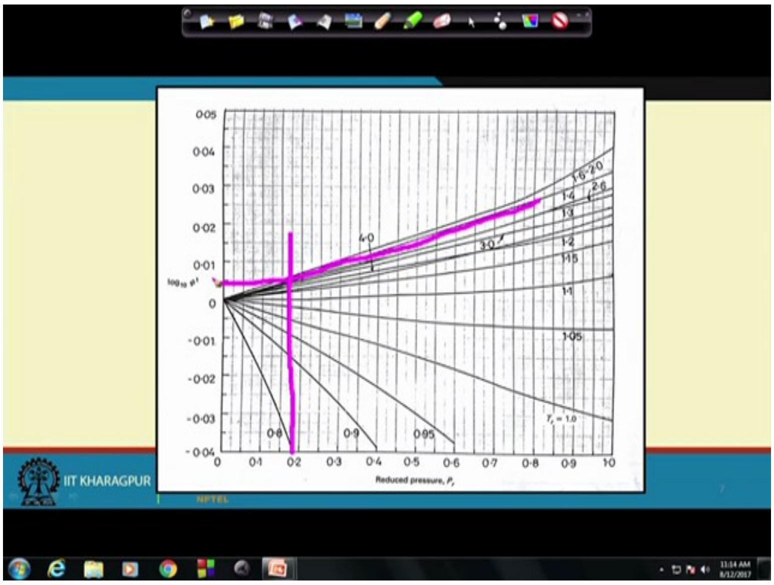

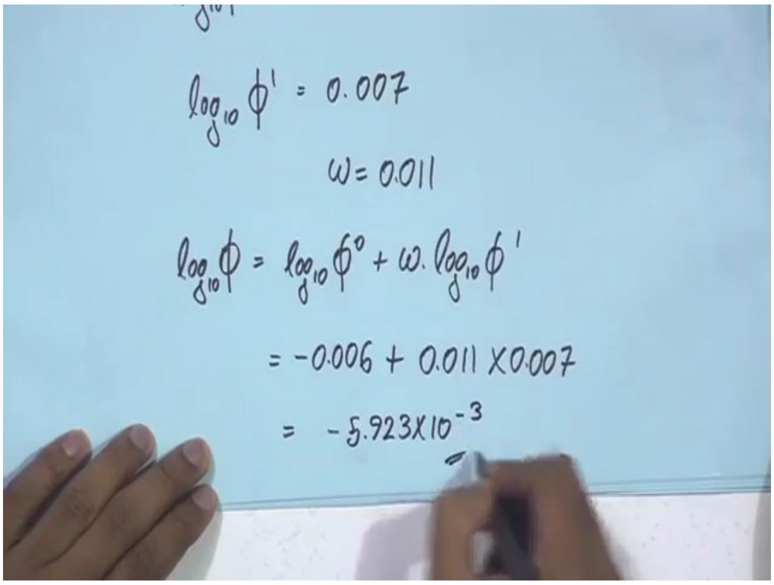

And in the same way we need to find out the value of log phi 1, we go to the next chart we start from 0.2 that is this point, so 1.6 curve is here it meet somewhere here and we get the value of log phi 1 as 0.007. So we know these two values, we know the value of acentric factor. So log phi and we get the final value of log phi as minus 5.923 into 10 raised to minus 3.

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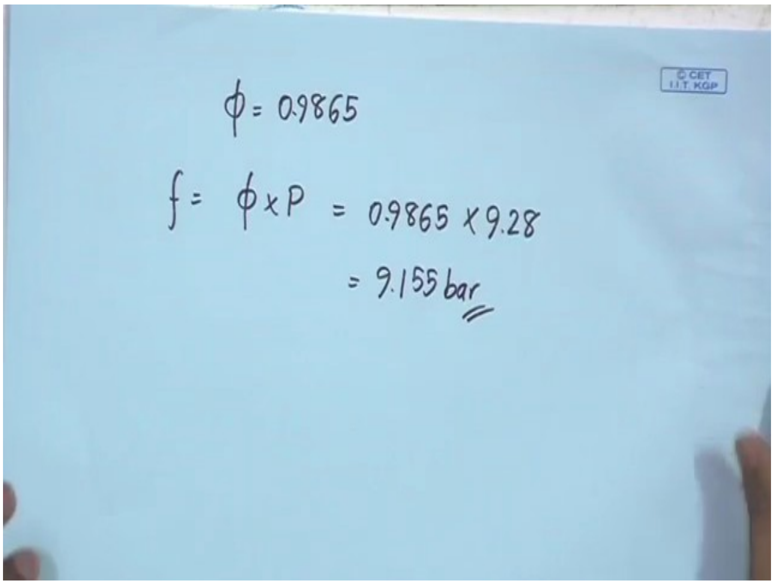

We take the anti-log so we get the value of phi as 0.9865 and we find out the fugacity as phi into P as we did in the last problem and that is 0.9865 into 9.28 is equal to 9.155 bar that is the value that we got. So we have almost familiarized with what we need to do when we get charts and when we get reduced temperature and critical temperature values, etc to find out the fugacity and fugacity coefficient.

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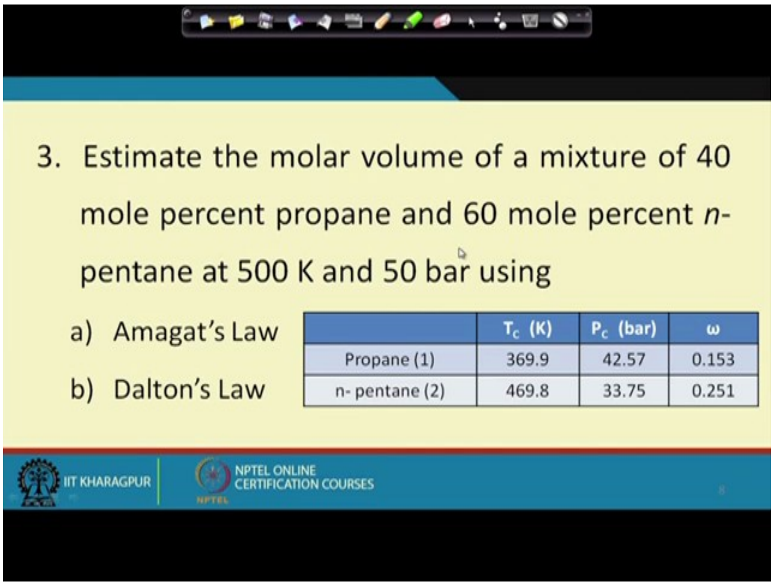

So we move onto the next problem, I read out the problem. Estimate the molar volume of a mixture of 40 mole percent propane and 60 mole percent n-pentane at 500 Kelvin and 50 bar using one Amagat's Law, two Dalton's Law. So the values of critical temperature, critical pressure and acentric factor all are given we do not need acentric factor here because we are dealing with two parameter model so we simply avoid these values.

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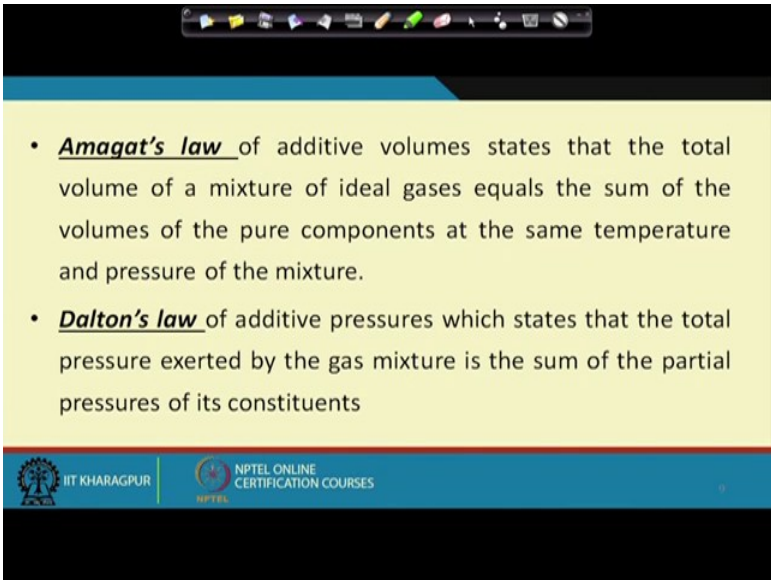

So before going into the problem we need it has been already taught but I just want to revise it little bit so that you will be understanding this problem better. We want to look back to what is Amagat's law and what is Dalton's law. So Amagat's law of additive volume states that the total volume of a mixture of ideal gases equals the sum of volumes of pure components at the same temperature and pressure as that of the mixture.

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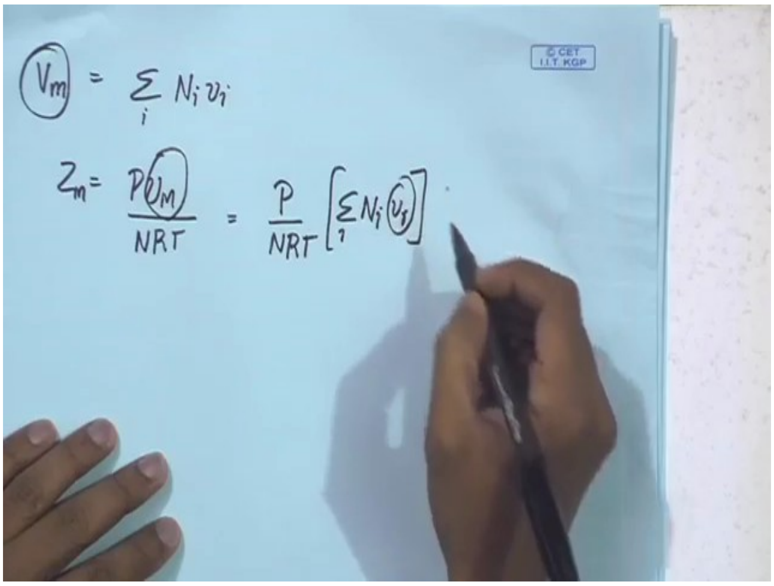

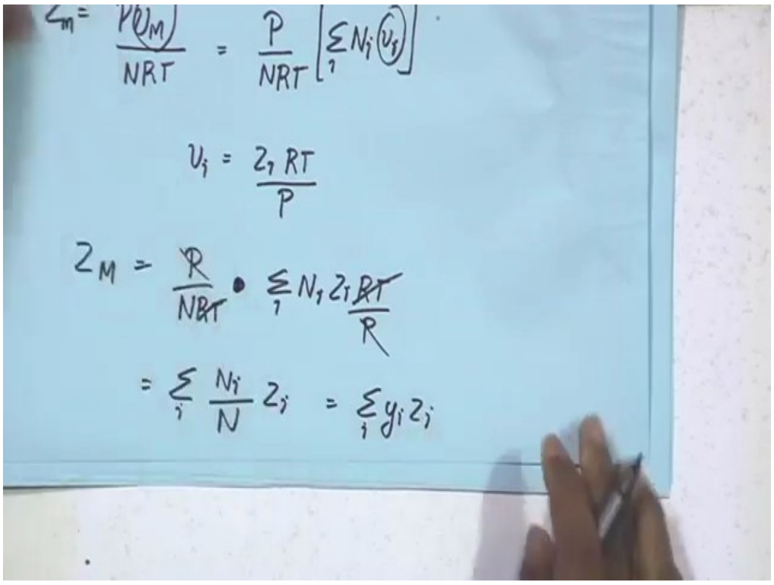

So basically it means the total volume of the mixture Vm it is summation of molar volumes of each components means the volumes of each component that constitutes the mixture. So we can write Zm that is the compressibility factor of the mixture as Pvm by NRT, where N is the total number of moles. We can substitute the value of m here and now here instead of Vi we can write, so we can substitute this value Vi here.

Therefore mixture compressibility factor becomes, this RT and this RT cancels out, this P and this P cancels out. This N comes into the summation part. We know Ni by N is nothing but the mole fraction of the component in the gas.

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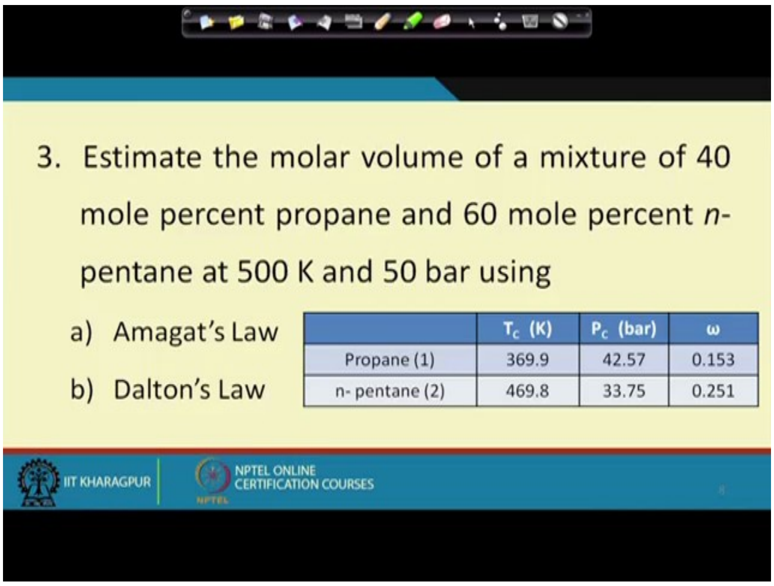

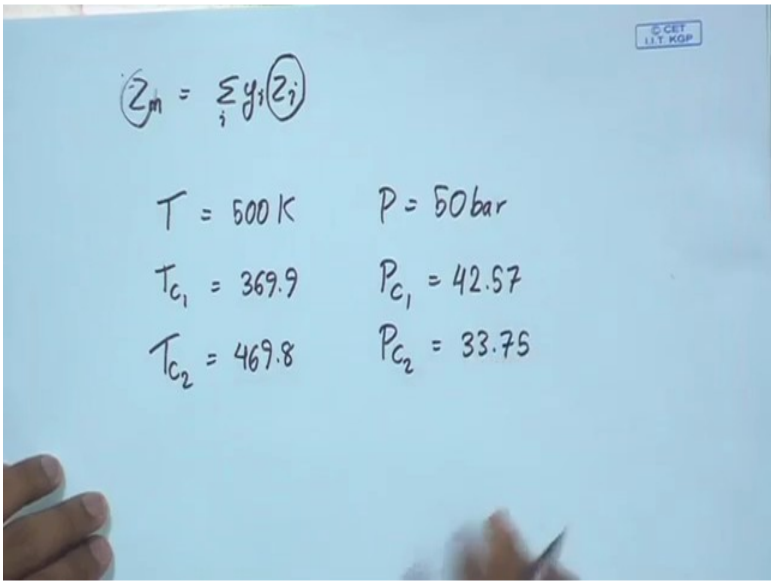

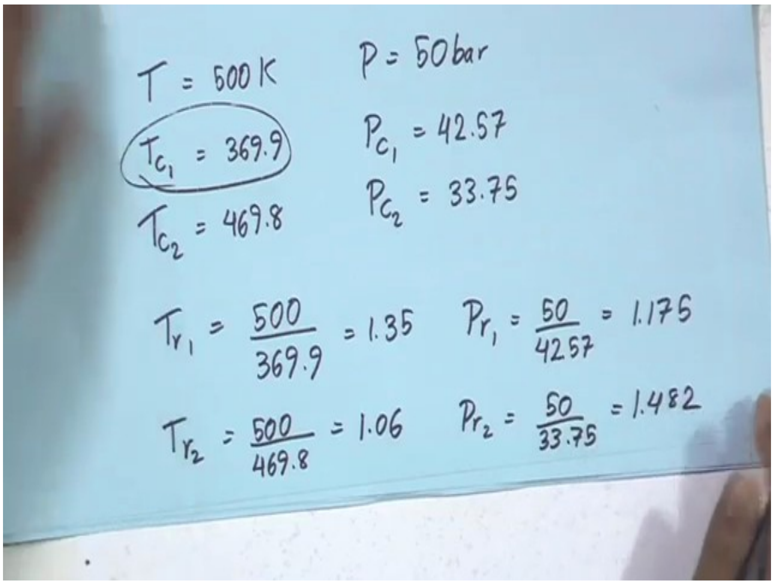

So I am writing it fresh here, here this is the compressibility factor of each constituent of that constitutes the mixture and here Zi is calculated at the same temperature and same pressure as that of the mixture where Zm is calculated. So let me go to the problem here we are having we are given temperature, temperature is 500 Kelvin, we are given pressure it is 50 bar, we are given critical temperature, critical temperature of component 1. I have mentioned propane as component 1 and n-pentane as component 2. So critical pressure temperature of component 1 is 369.9, component 2 is 469.8, critical pressure of component 1 is 42.57 and that of component 2 is 33.75, okay.

So we need to find out the reduced temperatures and reduced pressures of both these components, where 369.9 is the critical temperature of the first component we get the value as 1.35, Pr1 is equal to 50 by 42.57 we get the value as 1.175, Tr2 is equal to 500 divided by

469.8 that is 1.06, Pr2 is equal to 50 by 33.75 that is 1.482. So we got the value of Tr1, Tr2, Pr1and Pr2.

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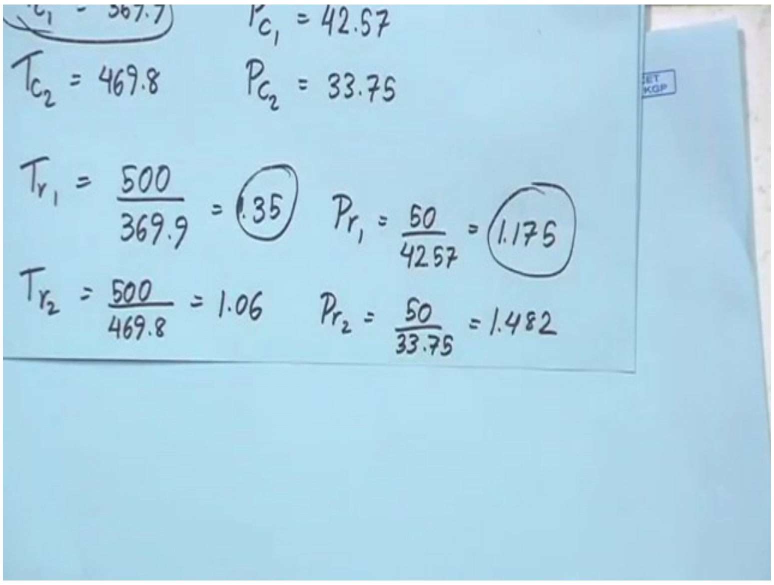

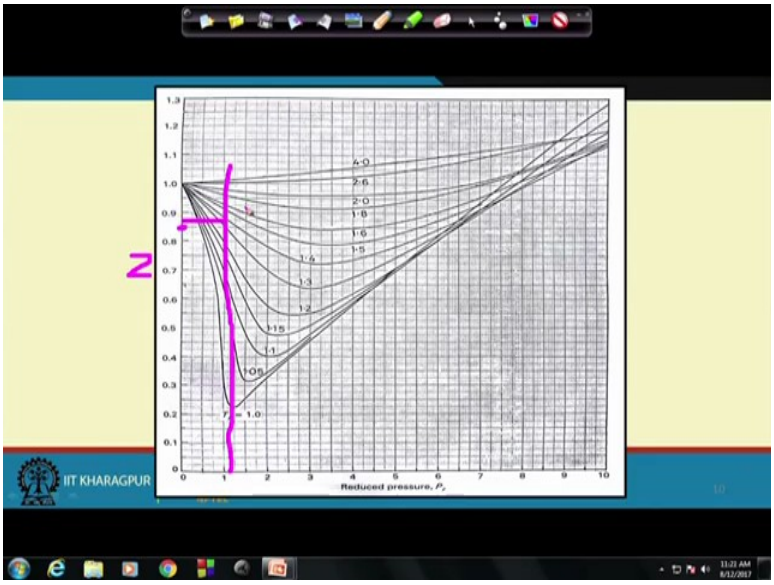

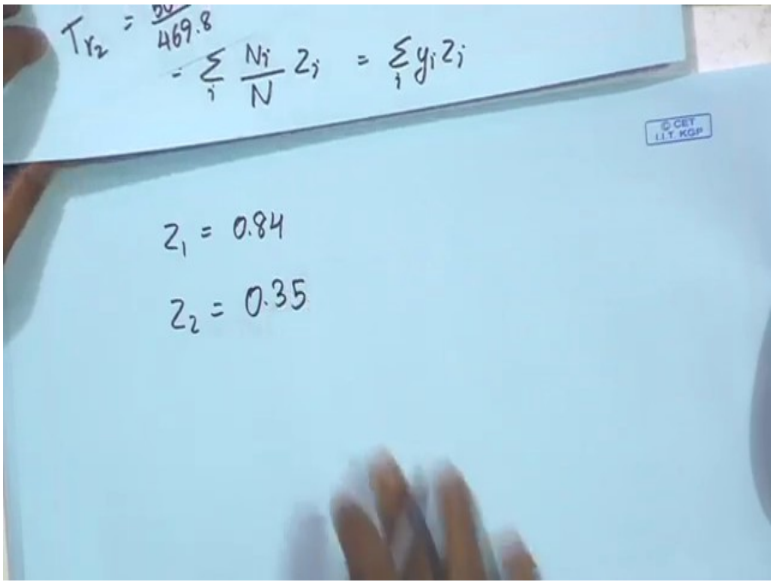

So now we have a chart and from there we need to find the value of Z1 and Z . This is the chart here reduced pressure is plotted at the x axis and all these lines corresponds different reduced temperatures and the y axis is Z, it is actually Z0 but since we are dealing with two parameter model I simply mention it as Z. So we need to find out Z1 and Z2 for both components.

So here we know Tr1 is 1.35 and Pr1 is 1.175, same in the same way as we have done in the last problem we just find out the value of Z1 from this graph 1.175 will come somewhere here we go up, 1.35 there is a value of reduced temperature is coming somewhere here. So we get the value of Z1 as I have made a small mistake here it will come somewhere over here. So the value of Z1 is 0.84, in the similar way we calculate the value of Z2 from the values of critical temperature and critical pressure for component 2 and the value of Z2 we got it as 0.35.

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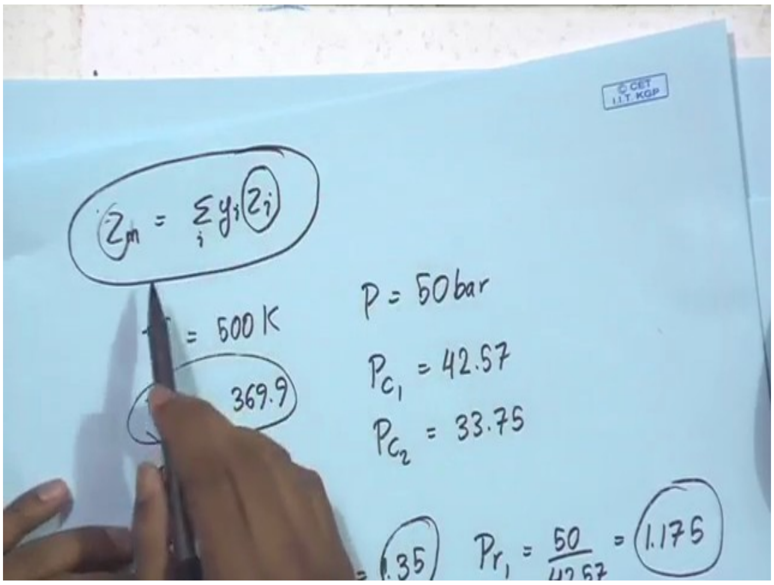

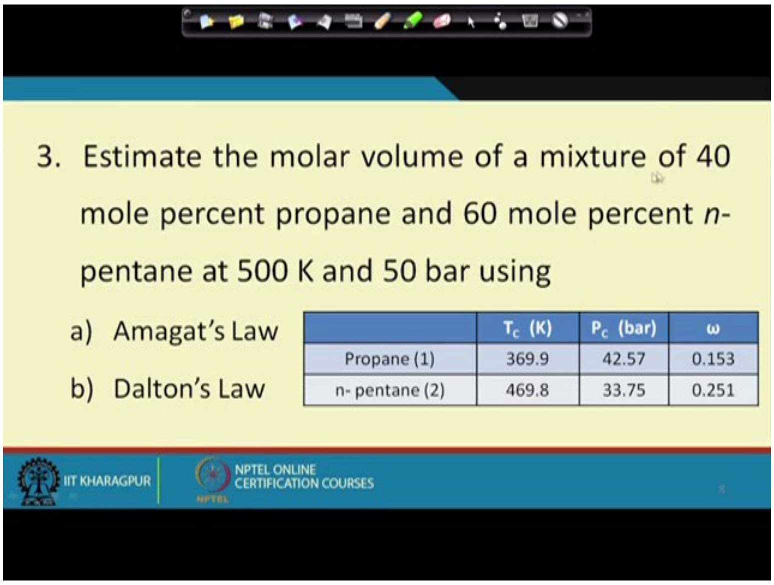

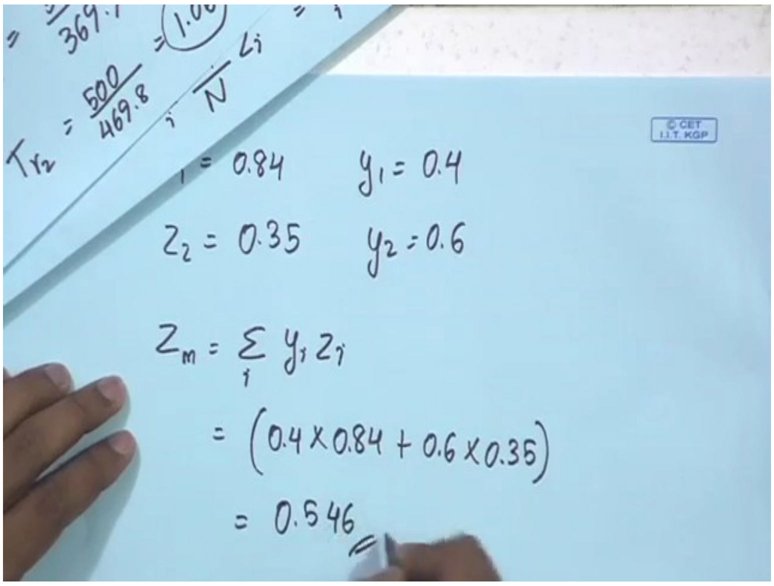

So here we know we have (calculated) we have proved it earlier for Amagat's law Zm is equal to summation of yi and zi. Here y1 here we know mole percent of propane is 40 and mole percent of n-pentane is 60, so y1 is 0.4 and y2 is 0.6. So we simply do the summation here 0.4 into 0.84 plus 0.6 into 0.35 and we get the value of Zm as 0.546.

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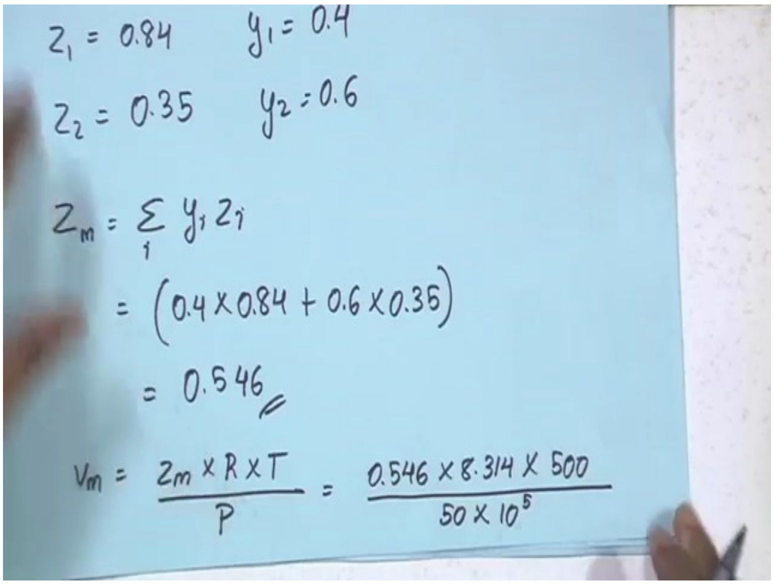

Now we need to find out the molar of volume of the mixture we know Vm is equal to Zm into R into T by P, so we know all the values P, T, R and everything we know we just substitute the values, the value of P is 50 bar we need to calculate in SI units, we need to put it in SI units. So we write it in Pascals 50 into 10 raise to 5 Pascal.

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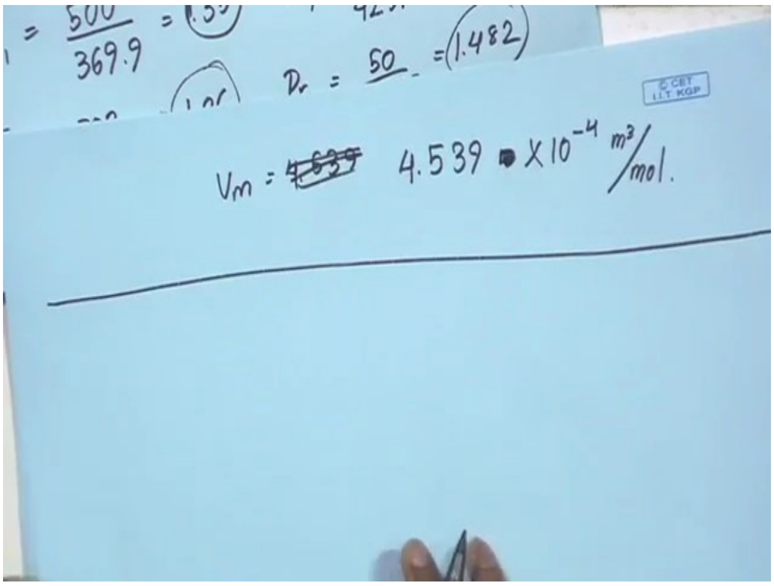

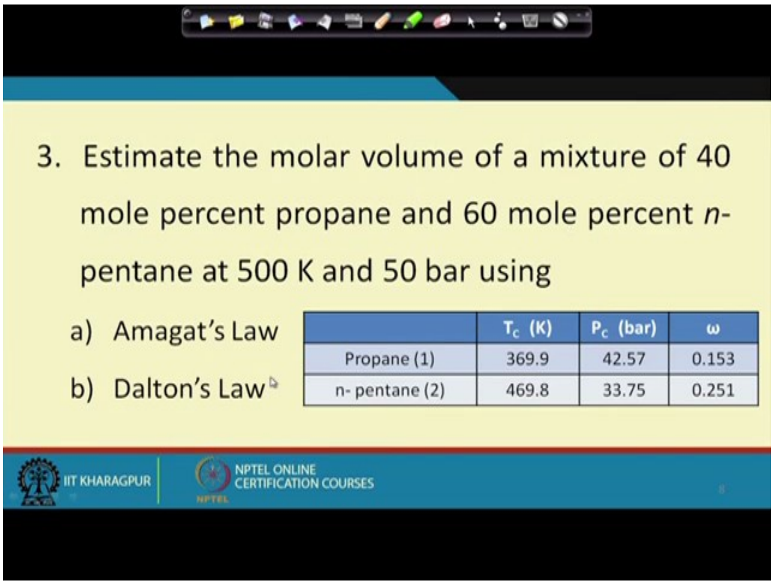

So we get the value of Vm value of Vm that is measured is 4.539 into 10 raised to minus 4 meter cube per mole, okay. Now we need to go to the second part of the problem that is the estimation of the molar volume of the mixture using Dalton's Law.

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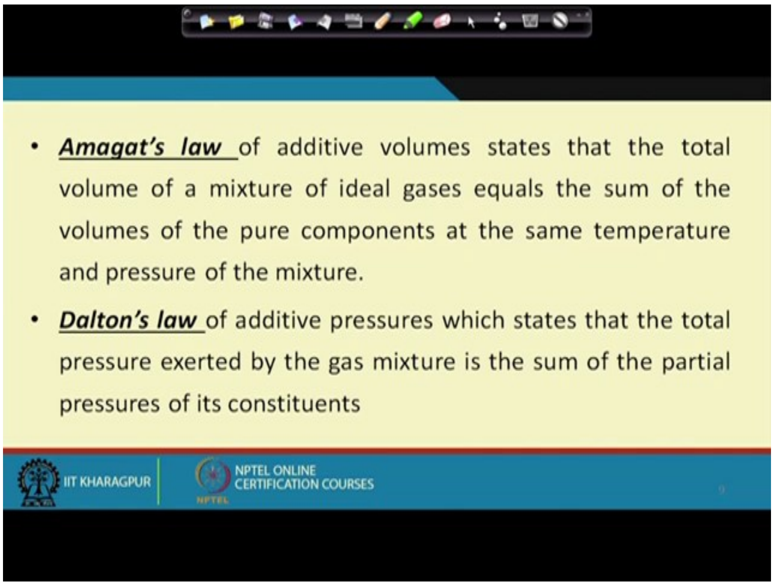

So Dalton's law of additive pressures states that the total pressure exerted by the gas mixture is the sum of the partial pressures of its constituents.

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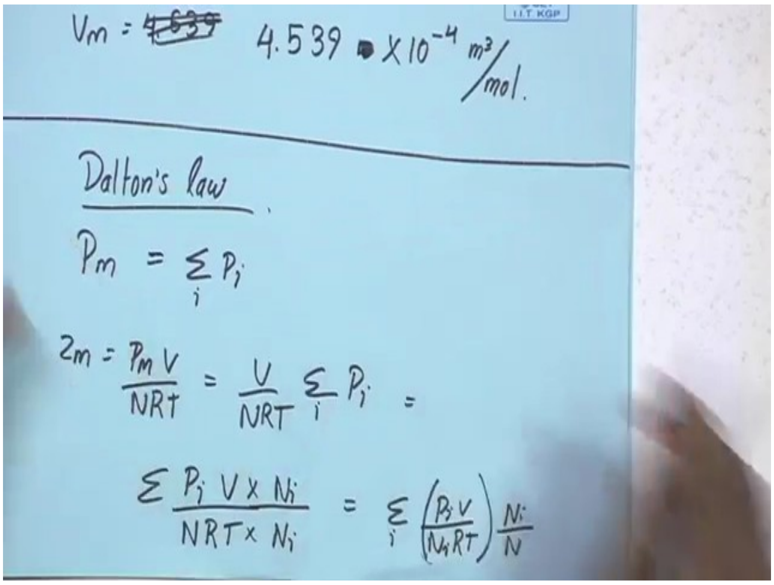

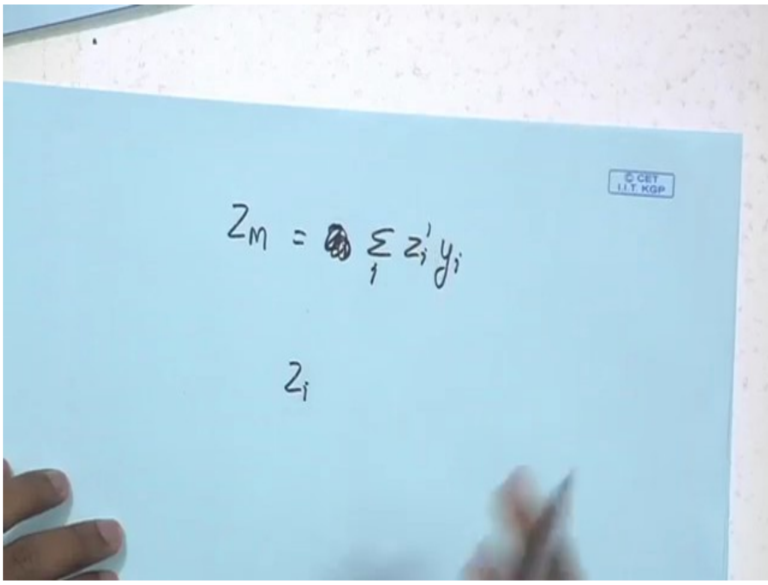

So what are we doing here total pressure of the mixture exerted by the gas mixture is the summation of the partial pressures Pi, so Zm we know it is Pm V by NRT which is equal to V by NRT, we substitute the value of Pm here and we bring these values inside the summation part, here we multiply both the numerator and denominator with an Ni and then we rearrange this this term. So we know this term corresponds to I am going over here over the next page.

This term we know it corresponds to Zi and Ni by N it corresponds to yi that is the mole fraction. So similarly we get almost a same expression that we got in Amagat's law in Amagat's law we got the means we got something like this but in Amagat's law the Zi that is calculated was at the same temperature and same pressure as that of the mixture but the Zi calculated in the case of Dalton's law it is as the same temperature as that of the mixture but it is at a different pressure.

The mixture pressure is different and this Zi is calculated at a pure component pressures, so we move with the problems. So before starting we need to estimate the values of Z1 and Z2, so for that we need to know the pure component pressures but that we do not know. So as an initial guess we take the pure component pressures as the partial pressures of each component.

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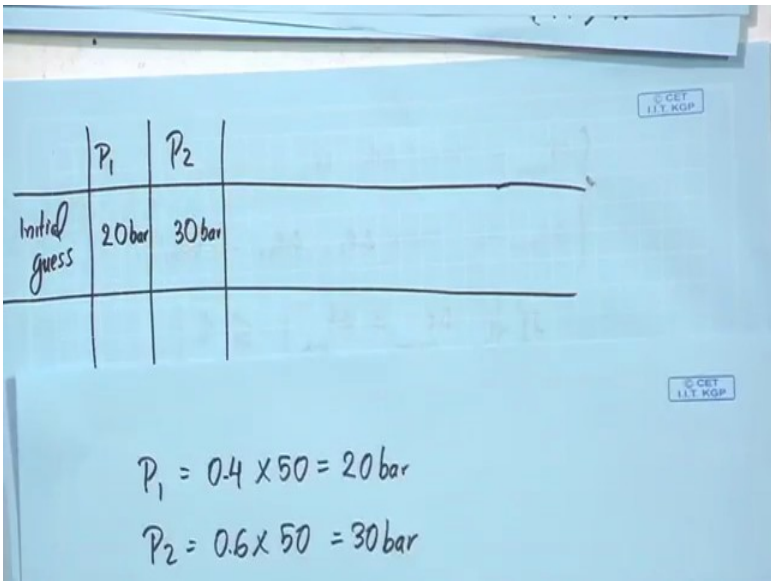

So P1 I am just writing it in the tabular form. So P1 we take it as the partial pressure of the component that is our initial guess that is 20 bar and P2 is 0.6 into 50 that is 30 bar. So we take those as our initial guess for pure component pressures.

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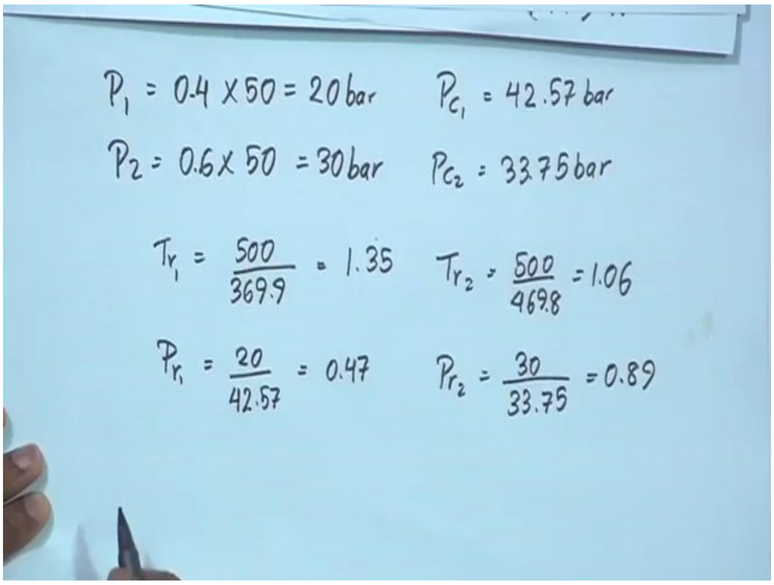

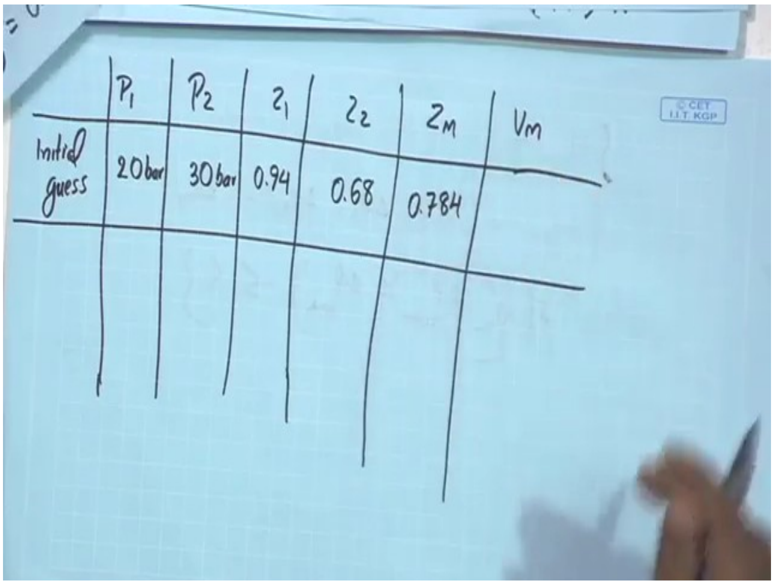

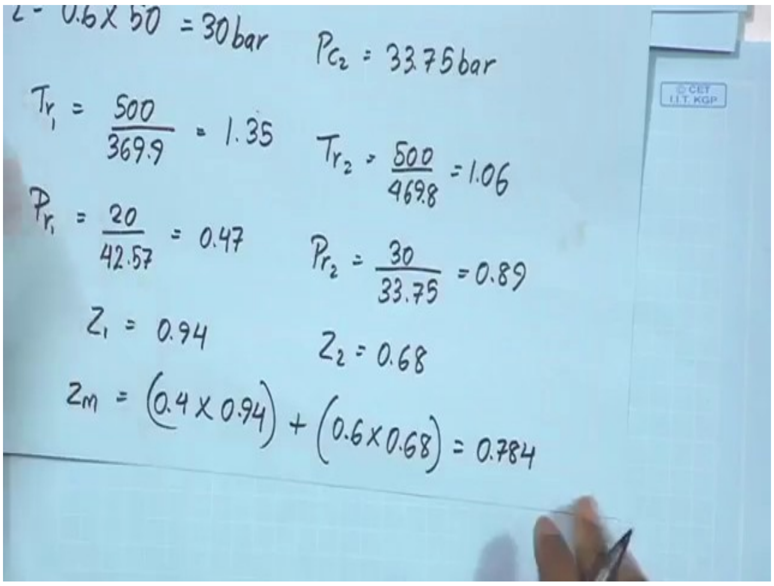

Now we know the Pc value we know the Tc value everything, so Tr reduced temperature value is same as that of the one we measured for the Amagat's law case that is 500 by 369.9 this is the critical temperature so that we got as 1.35. Now using these values these P1 and P2 values we know the Pc1 and Pc2 values. So we find out the Pr1 and Pr2 values, Pr1 value we got it as 20 by 42.57.

Now from these values we can calculate Z1 and Z2 using the chart that we have done earlier so I am not going into it I am simply writing down the value Z1 here we got it as 0.94, Z2 we got it as 0.68. So I am writing down the values here. Now from these values we can calculate Zm that is 0.4 into 0.94 plus 0.6 into 0.68 w get the Zm value as 0.784.

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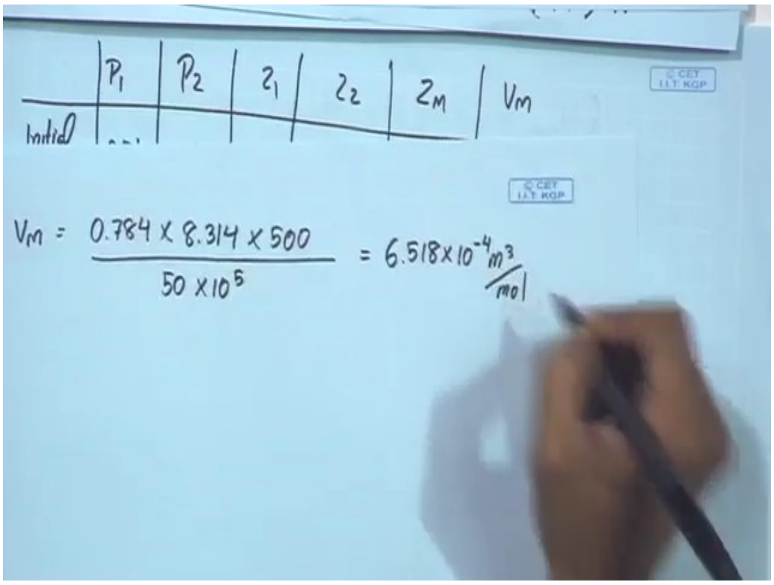

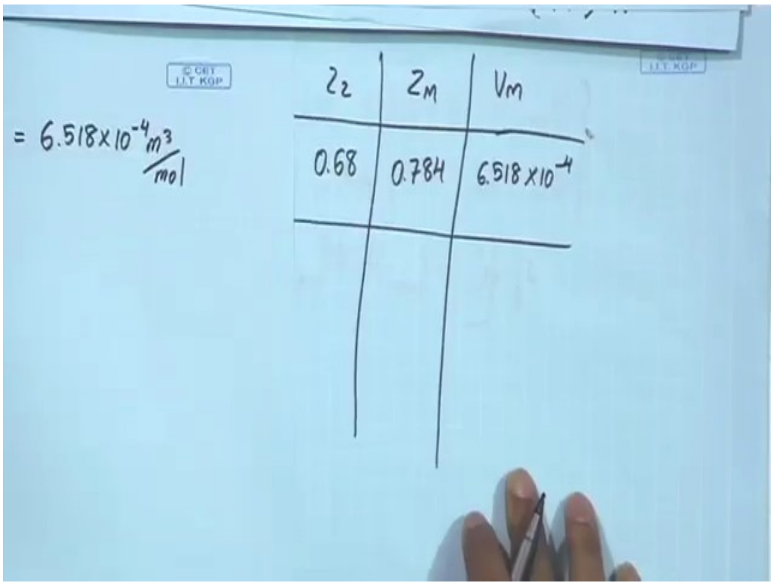

Now we need to calculate Vm, we do in the same way as we have done for Amagat's law we know the Zm value that is 0.784 into R 8.314 into T that is 500 Kelvin divided by the total pressure we get the value of Vm as 6.518 into 10 raised to minus 4 meter cube per mole I'm writing it here.

Now I told you earlier we have assumed that we assumed the pure component pressures as the partial pressures of each component. So that was our assumption we need to cross check whether our assumption was right or wrong.

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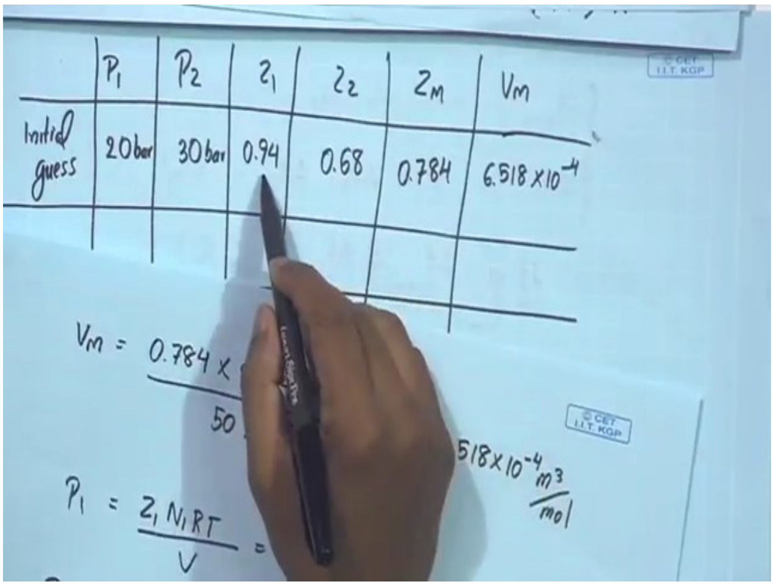

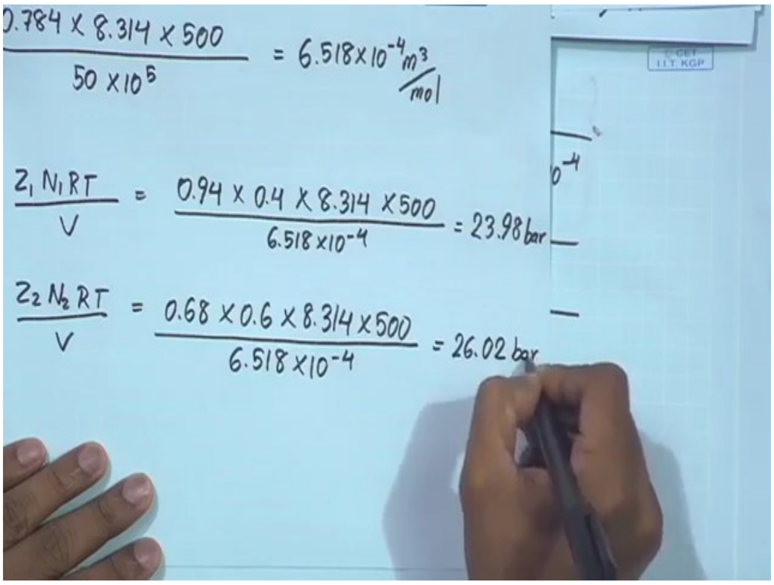

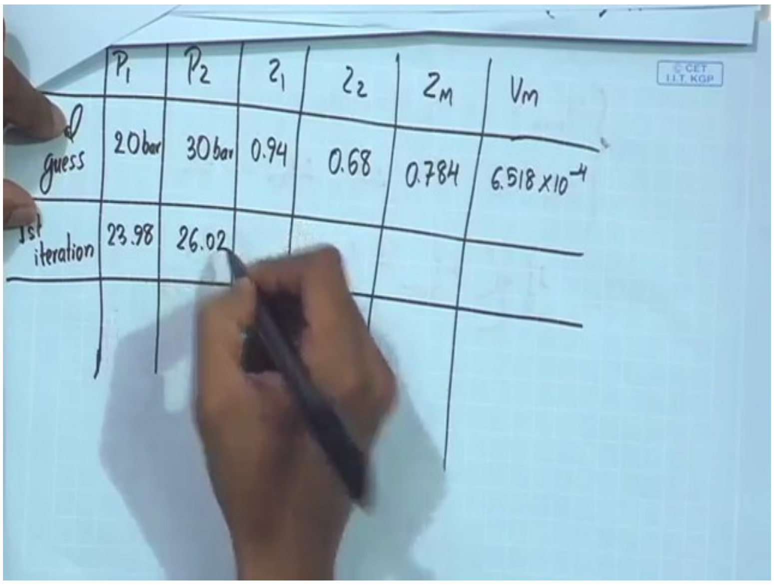

So we need to recalculate P1 value and P2 value using Z1 and Z2 values that we have got. So I am doing that, P1 you know it is Z1 N1 RT by V we assume one mole. So Z1 is 0.94 I am taking it from here, N1 is 0.4, R is 8.314 and T is 500 Kelvin and V it is the Vm value that we have got from here it is 6.518 into 10 raised to minus 4 and we get the value of P1 as we get the value as 23.98 bar I am writing here the value first iteration and we get the value of P2 in the similar way, we substitute these all these values Z2 we know it is 0.68, we get the value as 26.02 bar, I am writing down the value here.

So if we just notice we can find out that here there is a deviation from our initial guess around 4 bar deviation is there 20 to 23.98 and here also around 4 bar deviation is there 30 to 26.02. So our initial guess was not exact means it was not very good guess.

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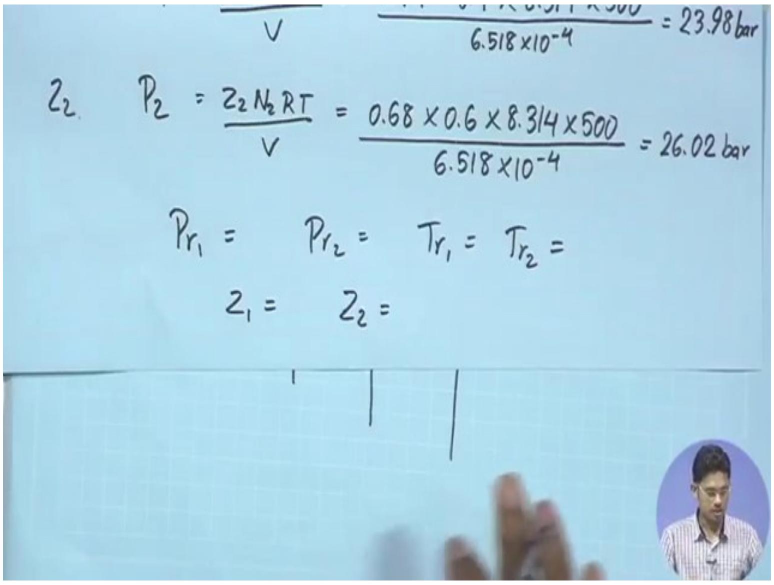

	P_1	P_2	z_1	z_2	Z_m	V_m
Initial guess	20 bar	30 bar	0.94	0.68	0.784	6.518×10^{-4}
1st iteration	23.98	26.02	0.93	0.73	0.81	6.734×10^{-4}

$$Z_m = (0.4 \times 0.93) + (0.6 \times 0.73) = 0.81$$

$$V_m = \frac{0.81 \times 8.314 \times 500}{50 \times 10^5} = 6.734 \times 10^{-4}$$

$$Z_m = (0.4 \times 0.93) + (0.6 \times 0.73) = 0.81$$

$$V_m = \frac{0.81 \times 8.314 \times 500}{50 \times 10^5} = 6.734 \times 10^{-4} \; m^3/mol$$

So we need to recalculate the whole thing with our (second) first iteration values, so we know P1, we know P2 we find out Pr1 again and we find out Pr2 again and from these Pr1 and Pr2 value we know the Tr1 and Tr2 values already that is the initial value itself there is no change for Tr1 and Tr2 values and from these values we use the graph and we find out our Z1 and Z2 again.

I am not going deep into the calculation because there is a time limit for me, so I am just writing down the values of Z1 and Z2 as calculated earlier, Z1 value it is point 0.93, Z2 value it is 0.73 and we can calculate Zm as I told earlier just a minute. So I am writing down the value Z1 the new Z1 value that I have got and Vm we know it is 0.81 that is the new value that we have got, so we get a new value for Vm that is molar volume of the mixture, write down the value here.

So we continue these iterations till we get least deviation between these P means these P values that is here we got deviation of 4 bars so these deviation reduces with iteration and finally we have to be satisfied with that point that where were these gap has come down to a very small value.

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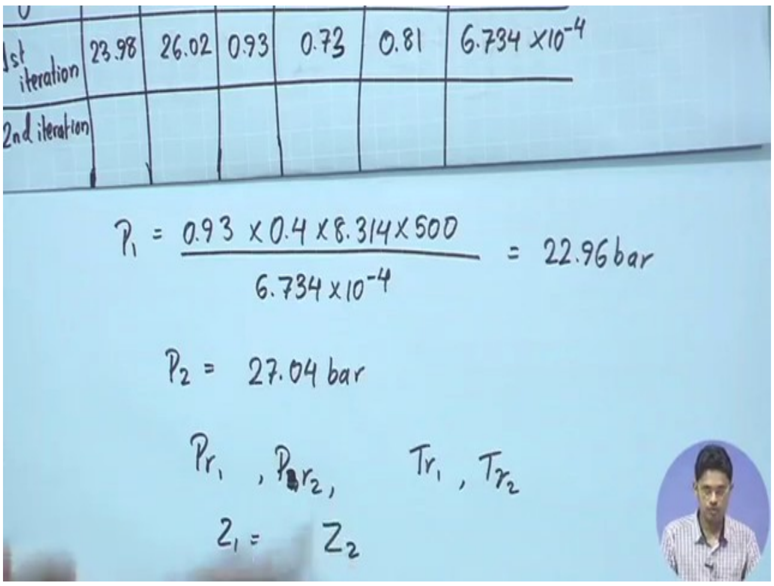

Now as we have got the value of Vm after our first iteration, so we need to do our second iteration. So we need to calculate P1 and P2 again from the new values of Z1 and Z2. So I am going to that here. The new value of Z1 is 0.93 and the new value of Vm is 6.734 into 10 raised to minus 4 and we get the new value of P1 as 22.96 bar, similarly we get the new value of P2 as 27.04 bar.

So we know the new value of P1, we know the new value of P2, we calculate Pr1, Pr2 again. The values of Tr1 and Tr2 are the same that we calculated earlier. So from the chart we can find out the new values for Z1 and Z2 we do that again.

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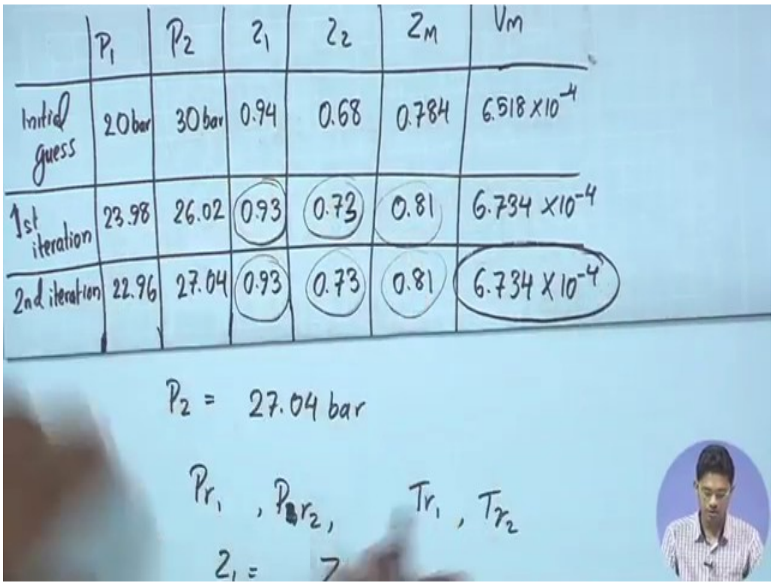

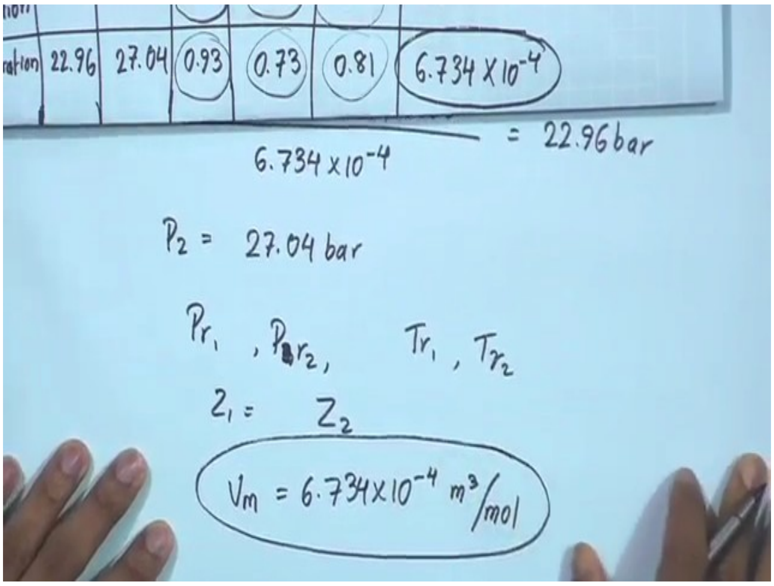

So we got the values of Z1 and Z2 as I am writing the values of P1 and P2 here, we did the calculations and we got the value of Z1 as 0.93 and Z2 as 0.73 we did the calculations and we found out the value of Zm as 0.81 and if we just simply compare we can see that here the value of Z1 is 0.93, here also it is 0.93, 0.73, 0.73, 0.81 and 0.81. So there is no difference after the (second iteration) means after the first iteration when we come to the first iteration to second iteration there is no difference in these values. These values are exactly the same.

And the value of Vm when we calculate it again we get it again as 6.734 into 10 raised to minus 4. So since there is no difference after this iteration we fix the value Vm as 6.734 meter cube per mole into 10 raised to minus 4 meter cube per mole. So this is how we calculate the molar volume of the mixture using Dalton's law.

So in this problem we have found out how we calculate molar volume of the mixture using Amagat's law as well as Dalton's law. So that is for that is all for this tutorial and if you are having any doubts regarding this problems just let us know we will be helping you, so that is all thank you, thank you so much.