Thermodynamics of Fluid Phase Equilibria
Dr. Jayant K Singh
Department of Chemical Engineering
Indian Institute of Technology, Kanpur

Lecture - 46
Examples of Fugacity of Liquids

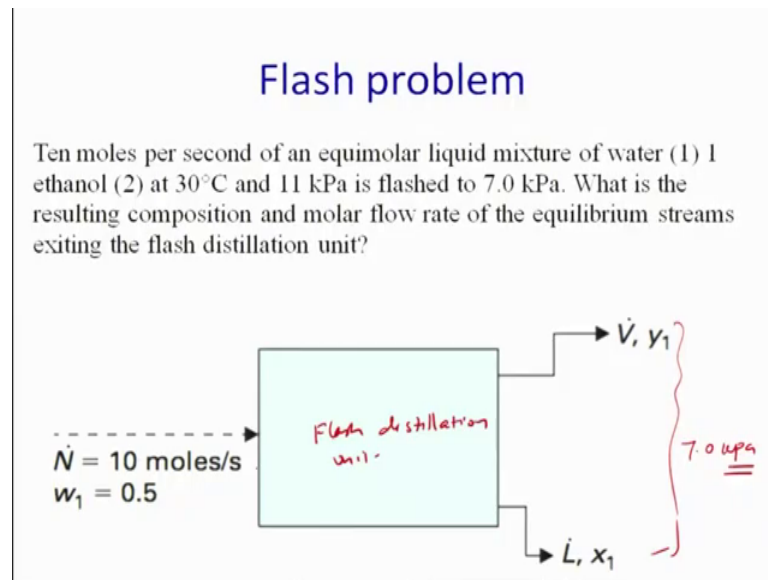Welcome back. In this lecture we are going to do some examples.

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This is a flash distillation problem and we would understand the importance of activity models ok.

So, what is the flash distillation? It is typically it segregates the liquid as a solution in liquid in vapor form ok. So, this is a problem which we have the 10 moles per second of the equimolar liquid mixture water and ethanol at 30 degrees Celsius and 11 kilopascal is flashed to 7.0 kilopascal. So, in other word where we are saying that you have this situation at 7.0 kilopascal right.
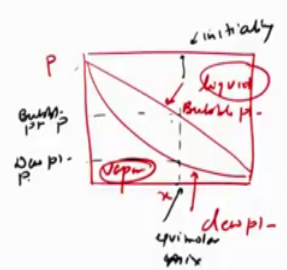
So, the question is what is the resulting composition and molar flow rate of the equilibrium streams existing the flash distribution unit which is this one ok. So, I mean it is not you know in reality it is not simple box there are many things in between. So, I am not going into details of the equipment structure, but our interest is basically to understand how to solve such a problem and there is nothing given here right.

So, the first important question is whether the system will flash at all. I mean that is the most important question like you know how do you know that the system will flash in a cell will cell separate, that is that is something which you have to understand ok. Is it going to be flash partially or will it flash completely to let us say vapor phase? So, how do you solve this problem?

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Let me first explain this. So, these are the questions which would be the first step if you want to solve such a problem ok. And in order to address that you need to pay attention to the basic phase diagram let us say this is a P x y diagram. So, we are talking about a generic diagram. So, let us say if I am using a concept from the Raoult's law then I will be able to get something like this ok, where the straight line is basically indicative of liquid saturation line ok.

So, this is sometimes also called bubble liquid this is a bubble point line. So, this is this is a liquid phase and this is a vapor phase this is a bubble point line and this is a dew point ok, so bubble and dew. So, first drop of dew is forming first bubble of vapor is forming.

Now, if you if you pay attention to this then let us say for a given concentration given in the system and you asking a question that whether is going to flash a partially or fully. So, for given composition, so in this case it is given equimolar. So, it is like 0.51 you will this would be for a given concession you have this if you draw a line here what are you going to get there is two pressures you are going to get, right. So, this would be your bubble point pressure correspond to equal composition this will be your dew point pressure ok.

And if the final structure final composition for this if the pressure there is in between that then essentially you are saying that is going to separate segregate in liquid and vapour. If

it is more than that if it is somewhere here then it will flash to liquid phase ok, if it is less it is a vapor phase. Now, currently it is in liquid phase. So, basically you are talking about from here whether it is going to flash or not.

So, this pressure whatever the pressure here with this pressure is above this the final one let us say this is 7 kilopascal right. So, if 7 kilopascal where the final one is here then it will not flash at all if it is somewhere here that will flash partially there, if it is here then it flash fully to vapor phase all right. So, this is the first step to identify what we are going to do and how I am going to solve this problem we should first to determine the bubble point pressure and dew point pressure for our mixture 30 degrees Celsius ok.

If the bubble point pressure is less than the system pressure if a bubble point pressure is less than the system pressure somewhere here we still have an equimolar liquid mixture ok. If the boiler point, so somewhere let us assume that. So, in order to understand let us assume that you were here right initially and finally, you know let us assume that you keeping the composition fixed if you which only changing the pressure if the pressure is a system pressure finally, is more than the bubble point then you will have a liquid mixture, but at a different pressure lower pressure that is what this statement is. If the bubble point pressure is less than the system pressure we still have an equimolar liquid mixture just at a lower point lower pressure.

Now, if the dew point pressure which is here is higher than the system pressure. So, this pressure is higher than the system pressure; that means, the finally, the system pressure is below this below this dew point pressure which means everything will flash to vapor. So, liquid completely goes to the vapor phase. So, that is a that is a there is a concept here ok.

So, if the dew point pressure is higher than the system pressure we have flashed all our mixture to a vapor and now, have an equimolar vapor mixture, you understand this part right. So, both scenario do not result in any separation which is the point of distillation. So, this is why it becomes an important to understand these pressure relations right. Now, that is where the phase diagram becomes an important.

So, what you need is basically a system pressure should be somewhere in between this in order to separate ok. Now, how do you solve this such a problem? You do not have anything other than this information right, but of course, for water ethanol you may find

a saturation pressure information from antoine equations which are available widely in the web and as well as many textbook. So, the first important thing is to actually find out your this bubble point pressure and dew point pressure ok. So, let us first look at it. System pressure the final condition is 7 kilopascal. So, the first thing which we are going to do is basically we will simply consider Raoult's law to start with ok.

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Now, you know that this if you add it you are going to get P total pressure P right. Now, how do you get. So, remove one is basically water and two is ethanol ok. So, the how you are going to get this one you are going to make use of antoine equation right. So, so using antoine equation ok.

So, if you use antoine equation from the test minimum different test books are available, you can also make use of NIST website a book where all this thermodynamics datas available. Then P 1 sat at 30 degree Celsius is 4.25 kilopascal and P 2 sat again at 30 degree Celsius is 10.56 kilopascal. So, using this if you add it up it becomes P y 1 plus P y 2 is equal to P this is your x 1 P 1 sat plus x 2 P 2 sat ok.

So, x 1 I know, x 2 I know. So, and P 1 sat I know here P 2 sat I know. So, if you plug in here this information this is 7.41 kilopascal which is greater than 7 kilopascal ok. So, what it says? This is what we what we obtain in this case the first important thing is what did we obtain here. This is a bubble point or is a dew point x here. So, we are talking

about a x liquid composition P corresponds to liquid composition at saturation. So, that would be your, if you look at it here that is going to be bubble point ok.

So, this is a bubble point pressure. So, this is a bubble point pressure which is above the system pressure which is nice because you wanted bubble point pressure to be to be higher than the system pressure, but of course, you also want your system pressure to be greater than the dew point pressure.

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Step 2

Since the bubble-point pressure is above that of the system pressure, we know that we do not have all liquid. Next, let's determine the dew-point pressure to see if we have just a vapor or both liquid and vapor

Once again, we use Raoult's law to model our system, but now we use it to calculate the dew-point pressure.

Write definition of Raoult's law

$$P y_1 = x_1 P_1^s$$
$$P y_2 = x_2 P_2^s$$

So, let us first again find out what is a dew point pressure. So, since the bubble point pressure is above the system pressure we know that we do not have all liquid. So, either it is a partially liquid or completely gas vapor phase.

Next let us determine the dew point pressure to see if we have just a vapor or both liquid and vapour. Once again we will be going to use Raoult's law to model our system, but now, we use it to calculate dew point pressure ok. So, we are going to write again the same way that we are going to write P y 1 x 1 P 1 sat, P y 2 is equal to x 2 P 2 sat, but then we will get rid of x here ok.

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$$\frac{Py_1}{P_1^s} = x_1 \quad ; \quad \frac{Py_2}{P_2^s} = x_2 \quad ; \quad \frac{Py_1}{P_1^s} + \frac{Py_2}{P_2^s} = 1$$

$$\text{or } P_{dew\,pt} = \cfrac{1}{\left(\frac{y_1}{P_1^s}\right) + \left(\frac{y_2}{P_2^s}\right)} = \cfrac{1}{\left(\frac{0.5}{4.25\,kpa}\right) + \left(\frac{0.5}{10.5\,kpa}\right)}$$

$$= 6.06\,kpa < \underline{7}$$
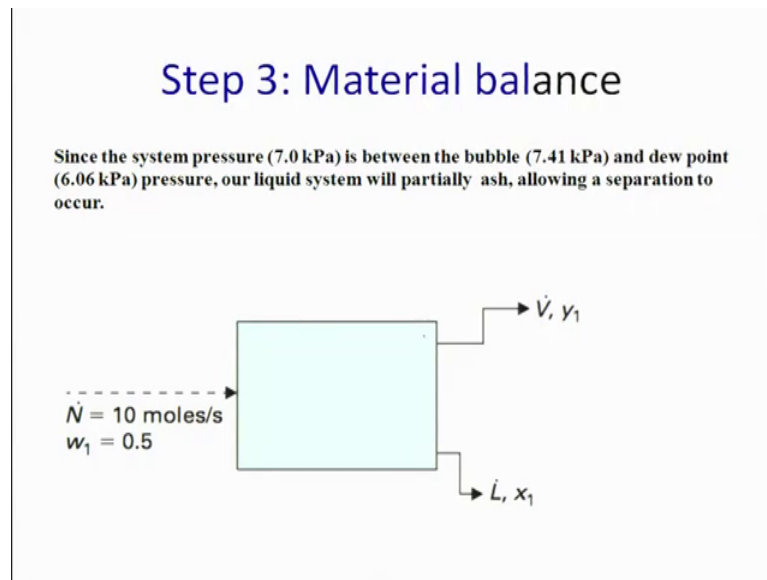
Since $P_{dew\,pt} < 7.0\,kpa < P_{bubble\,pt}$

$\Rightarrow$ Separation will occur

So, the way we are going to do is P y 1 by P 1 sat is equal to x 1 and P y 2 P 2 sat is equal to x 2 and x 1 plus x 2 is equal to 1; that means, P y 1 by P 1 sat plus P y 2 by P 2 sat is equal to 1 or P is common here this is nothing but y 1 by P 1 sat plus y 2 by P 2 sat ok.

So, this is the expression of dew point right. So, I can now, plug in this expression. So, this is 0.5 by 4.25 kilopascal that is again 0.5 by 10.56 kilopascal and this comes out to be 6.06 kilopascal which is, less than 7. So, this tells you that since the system pressure is greater than the P dew and P bubble in other and less than P bubble point ok, this means separation will occur ok. I mean this is given by Raoult's law concept right.

Now, the next question is how do you get the composition. So, once we have formulated this the next thing is to do a material balance all right.

Step 3: Material balance

Since the system pressure (7.0 kPa) is between the bubble (7.41 kPa) and dew point (6.06 kPa) pressure, our liquid system will partially ash, allowing a separation to occur.

$\dot{N} = 10$ moles/s
$w_1 = 0.5$

$\dot{V}, y_1$

$\dot{L}, x_1$

So, you can write down the equation of material balance right. Now, you have with all the information. So, let me just write down. So, this is here N dot is equal to V dot plus L dot right and then you can do individual one of the component balances.

Overall Balance: $\dot{N} = \dot{L} + \dot{V}$

Comp   1 $w_1 \dot{N} = x_1 \dot{L} + y_1 \dot{V}$

Four unknowns

$10 \frac{mol}{s} = \dot{L} + \dot{V}$ — ①

$(0.5)(10 \frac{mol}{s}) = x_1 \dot{L} + y_1 \dot{V}$ — ②

$7 \text{ kpa} \cdot y_1 = x_1 \cdot 4.25 \text{ kPa}$ — ③

$7 \text{ kpa} (1-y_1) = (1-x_1) \, 10.56 \text{ kPa}$ — ④

Excel   Solver $\dot{L} = 7.11$ mol/s
$\dot{V} = 2.89$ mol/s
$x_1 = 0.56$
$y_1 = 0.34$

Overall of balance N dot is equal to L dot plus V dot and that is a component one balance we do w N and dot is equal to x 1 L dot plus y 1 V dot ok.

So, there are 4 unknowns right. So, we can try to 4 unknowns then we must have also 4 equations we have to write right. So, let us write down. So, one is of course, 10 moles

per second is equal to L dot plus V dot then you have 0.5, 10 moles per second is equal to x 1 L dot plus y 1 dot v. Now, since it is a saturation we are going to use the conditions of 7 kilopascal multiplied y 1 at the final exit P into y 1 is equal to x 1 and saturation for individual component this is for component 1 and 7 kilopascal 1 minus y 1. So, basically I am just writing down the Raoult's law for component 1 and 10.56 kilopascal.

So, you have 1 2 3 4, 4 equations 4 unknowns. So, you should be able to solve this. Now, in order to solve this one you have to make use of some kind of program ok. So, one of the simpler way to handle is to use excel solver ok, you can write a MATLAB code also it will be very straightforward to do that ok. So, if you do this exercise and the final expression or answer comes out to be something like this. So, you can check this at your home ok. So, this is the final expression.

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Recap

To recap, we have taken 10 mol/s of an equimolar liquid mixture of water (1) and ethanol (2) at 30°C and 11 kPa and flashed it to 7.0 kPa.
A liquid stream exited the flash distillation unit at 7.11 mol/s with a composition of 56% (by mole) water, while a vapor stream also exited the flash distillation unit at 2.89 mol/s with a composition of 34% (by mole) water vapor.

Thus, we have somewhat separated our equimolar liquid mixture into a liquid portion that has an enhanced water composition and a vapor portion that has an enhanced ethanol composition. The more volatile component (ethanol) is concentrated in vapor phase.

So, let us recap what we did. So, we have taken 10 mole per second of an equimolar liquid mixture of water and ethanol at 30 degree Celsius and 11 kilopascal and flash it to 7 kilopascal. A liquid stream exited the flash unit at 7.11 will moles per second with a composition of 56 percent water while a vapor stream also exited the flash distillation unit at 2.89 moles per second with a composition of 34 percent by mole water vapour.

Thus, we have somewhat separated our equimolar liquid mixture. Into a liquid portion that has an enhanced water composition and a vapor position that has enhanced ethanol

composition. The more volatile component which is ethanol in this case is concentrated in the vapor phase that is what you expect ok. So, everything is beautiful right.
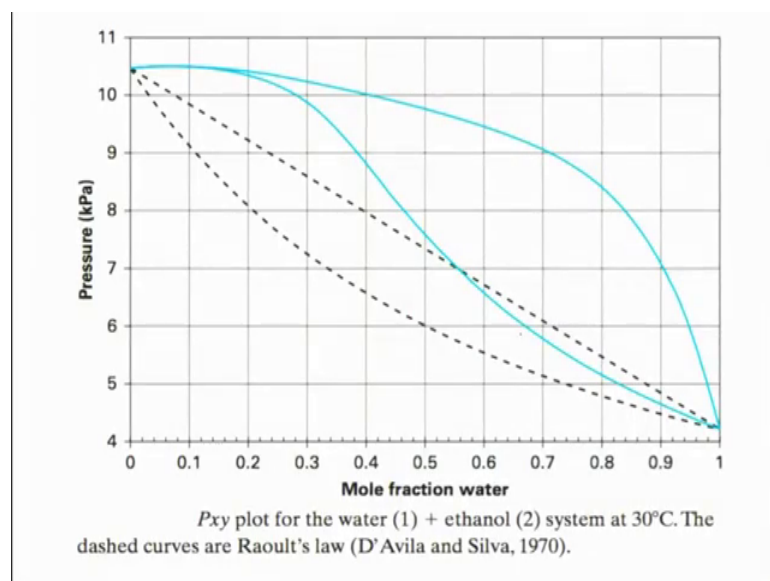
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Reality?

In reality, the recap provided is not what happens. Why?

In reality what happens in reality the recap provided is not what happens and why, so that is important. So, everything looks you know mathematically correct, you know there is some, but beautifully we segregated it, but this is not what the reality happens I am. So, in reality at this condition phase suppression will not occur. So, let us look at why.

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Pxy plot for the water (1) + ethanol (2) system at 30°C. The dashed curves are Raoult's law (D'Avila and Silva, 1970).

So, this is the pressure and composition of mole fraction it is not as a trope one if you look at this dashed line this is the phase diagram due to Raoult's law, but this the blue line the solid blue line is basically the real phase diagram from the experiment ok.

Now, we are talking about 0.5 ok. So, this was initially 11 and 0.5 right, and if you look at the system pressure is 7. So, what do you see? So, it will flash completely to vapor they do not face separate. If you had used Raoult's law of course, it shows that this system pressure is between the dew point and bubble point pressure, but in reality it is system pressure is below the dew point pressure and that is the reason that the work which we did will not be realized in reality it will flash compared to vapor from the liquid to vapor it will go.

So, which essentially means that knowing that water in ethanol is not an very simple system ok, it hydrogen bonds also we went ahead and used Raoult's law as a model which was in fact, not appropriate. So, knowing this we should not have use that. And that is something which is important. And this is an example where we should conclude that just because a model provides an answer it does not make it right answer ok.

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Conclusion

As is illustrated through Example, models relating the composition of the liquid and vapor phases are needed to solve flash problems when no experimental data exists. However, just because a model provides an answer, it doesn't make it the right answer. The chemical engineer is tasked with identifying what models to use and when to use them in order to make reasonable estimations for analyzing processes. Here, we already knew that the water-ethanol system would not behave as an ideal solution. Thus, using Raoult's law as a model for this system was, from the start, not a reasonable strategy, and this was validated in comparing the model results to that of experiment.

The chemical engineer is tasked with identifying what models to use and when to use them in order to make reasonable estimation for analyzing processes. Here we already knew that the water ethanol would not behave like an ideal solution ok. So, here we already knew that the water ethanol system would not behave as an ideal solution thus

using Raoult's law as a model for this system was from the start not a reasonable strategy and this was validated in comparing the model results to that of experiment. So, this is something which we can conclude based on this exercise.

So, the important thing is the models are important because it helps us to solve problems when the experimental data exists, but having a bit of understanding of the system would help you to find out the right model because there are lot of people who have already looked into the model, analyze the model, and quantified the model in terms of the appropriateness of the type of the systems which it works well. So, using that queue one should be able to choose the right kind of model for a given system.

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Now, let us see how we can address this part using a modified Raoult's law ok, where basically we are going to consider the liquid phase is non ideal and hence we bring in the gamma ok.

So, now, again we going to put it in a different one, but here instead of water ethanol we are going to consider different system. So, let us look at the problem again So, here is a 10 moles per second of an equimolar mixture of methyl ethyl ketone and toluene is flashed from 760 millimeter Hg to 460 millimeter Hg at 75 degree Celsius. You know experimentally that the infinite dilution activity coefficient of methyl ketone, methyl ethyl ketone in toluene is 1.44 at this temperature. Likewise you know that the

experimental value for the infinite dilute activity coefficient of toluene in methyl ethyl ketone is 1.33 at this temperature. So, these are the information is given.

Solve for the composition and amount of each equilibrium phase as a result of the flash if the liquid is treat as an ideal solution, if the liquid is treated as a model by two parameter Margules equation ok. So, this is the problem which we have So, this is, so the point is I am not taking it is basically this is the given statement in the problem.

So, let us try to solve see what we can make use of it ok. Of course, you can maintain the temperature also, but usually temperature will vary ok. But let us look at this problem again and then see whether what you are making is going to change anything or not.

So, what is saying that is 460 mmHg at 75 degree Celsius that is the condition at the flashed it all right.

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So, now, in order to solve this you must ask the question does the system flash at all does it flash partially, does it flash fully ok, and then since the first part is that if you want to use the Raoult's law model let us start with that that will be the first part.

So, again we will be using Raoult's law and the first question is basically we are going to find it the bubble point and dew point pressure ok. So, let us look at the bubble point ok. And you use again the you know antoine equation from the literature you find out this information again you can take a look at first NIST website for the details. So, this is the

saturation pressure at 75 degree Celsius. So, we are looking at the final condition. So, the emission elected temperature may change, but we are looking at the final temperature final the system conditions.

So, P 2 sat is given and this is also given. So, once this is given you can find out the pressure. So, this pressure is 0.5 657.6 remember g plus 0.5 244.3 mmHg it turns out to be 450.9. Now, this is the bubble pressure above point pressure. And what is the pressure given here? It is 460 mmHg.

So, basically this is less than the force extreme. What is that mean? So, P bubble point pressure is less than P system, which means, so this is below the bubble point that oh you are talking about pressure. So, this is 450 is below the system pressure thus it will not flash that is given by the Raoult's law model, so no suppression ok.

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The bubble point pressure (450.9 mmHg) is below the system pressure (460 mmHg), thus the system will not flash and no separation will occur. The material balance is trivial as we still have an equimolar liquid mixture of methyl ethyl ketone and toluene, and part (a) of the problem is solved.

Now, let us look at this is what is being said the bubble point pressure is below the system pressure the system will not flash and no suppression will occur. So, everything, so that is the material balance is trivial as we still have an equimolar liquid mixture of this and the party of the problem is solved.

What about the if you had used modified Raoult's law? Again if you had used modified Raoult's law will the system behaves the similar way as as you have evaluated using ideal solution conditions. So, in order to do that we write down again the gamma 1 x 1 P 1 sat. So, remember this if you are using Raoult's modified Raoult's law it is going to be P y 1 is equal to gamma 1 x 1 P 1 sat, right. So, this is a modified Raoult's law.

Here the vapor phase is considered to be ideal the liquid phase is non-ideal and basically using the activity as now, the corrections to the non ideal ideality. So, P would be gamma 1 x 1 P 1 sat plus gamma 2 x 2 P 2 sat ok. So, this is the basically the bubble point pressure which you have to calculate.

Now, what is given to us is we have to we have to use two state Margules equation. If you look at the question two parameter Margules equation let me first write down what is the two parameter Margules equation. It is basically nothing, but g of e by RT is x 1 x 2 A 21 x 1 plus A 12 x 2. So, you can say A and B also does not matter, but this is the one which I am going to use now, ok. So, this is the two parameter.

Now, if you make use of the fact that from here you can get basically ln gamma 1 by taking by connecting the law gamma 2 the partial derivative of n times moles time g and t with respect to g and i. So, log of gamma 1 is going to be x 2 A12 plus 2 A 21 minus A 12 x 1, similarly log of gamma 2 is x 1 square A 21 plus 2 A 12 minus A 21 x 2 all right ok.

So, the question is how do you find A 12 and A 21. If you look at the question here the question of what is given to us is also the infinite dilution. So, if you use this infinite dilution information let us say plugging x 1 to be 0 which means basically x 2 is equal to 1. So, if you consider x 1 to 0 which sorry x 2 yeah x 1 to be 0 which means infinite dilution which means x 2 is equal to 1 then ln gamma 1 infinity would be A 12 right.

So, in other word in other word we are saying that ln gamma 1 infinity is limit x 1 goes to 1 and then gamma 1 which is nothing but A 12 ln gamma 2 infinity is limit x 2 goes to 1 ln gamma 2 is A 21 and this information is already given.

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So, this is ln gamma 1 infinity is given in the problem statement. So, this is going to be log of 1.44 which is 0.3354 and this is going to be log of 1.33 which is 0.2846, ok.

First one, it should be x 2 tending towards one and this would be x 1 tending towards one ok, all right. So, you have this information. So, now, we can plug in this here in this expression of bubble pressure point bubble point pressure this is going to be gamma 1 x 1 P 1 s plus gamma 2 x 2 P v 2 s ok.

So, what is the; now, this information is there. So, what is your gamma 1 at 0.5 x 1 is 0.5 is 1.074. Gamma 2 at x 1 is 0.5 is 1.095. Basically at equimolar mixture you have this information you will plug in here. So, this will become 1.074 0.5 657.6 mmHg plus 1.095 0.5 243.3 mmHg. So, this is going to be 486.9. So, which is basically the bubble

point pressure it tells you that it is above the system pressure ok. So, which essentially still does not address our problem; So, we will be also finding out the dew point pressure.

So, we use again the dew point pressure to find out and so if you considered again the modified Raoult's law. So, it is going to P y 1 by gamma 1 s P 1 s is equal to x 1 right, P y 2 by gamma 2 P 2 s is equal to x 2. So, here we are going to find out the y's, so essentially the dew point right. So, we are going to get P 1 y 1 plus gamma 1 P 1 sat plus P y 2 gamma 2 P 2 sat is equal to 1, from here we can find out the pressure.

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So, P is 1 by y 1 by gamma 1 P 1 sat plus y 2 gamma 2 P 2 sat and if you plug in here 0.5 the gamma 1 this turns out to be 338.2 milli Hg. So, it tells you that the system pressure ok, it is greater than P dew point and less than P bubble point ok. So, basically tells you in between it is lying and thus now, this will mean that this is phase segregated which was not able to captured by the Raoult's law thing.

So, you again write down the energy balance ok. So, you have 10 milli moles per second is equal to l plus V dash, 0.5 10 millimoles per second this is going to be x 1 y plus y 1 v 1. And then again you are going to use that the Raoult's modified law where we are going to consider first the pressure P 460 mmHg y 1 and this is going to be 460 y 2 and this is going to be x 1 gamma 1 P 1 star ok.

So, you know x 1 sorry you know your P ones sat the gamma. You can now, write out in terms of exponential, so gamma is this right. So, gamma 1 would be exponential of this term. So, I am going to write here simply the exponential 1 minus x 1 square A 12 plus 2 and similarly here 1 minus x 1 244.3 mmHg exponential of basically the terms which you see it here ok, here. So, this way you have 4 equations and 4 unknowns. So, if you solve it using excel or MATLAB you should be able to get the following answer ok.

So, this is what I wanted to discuss in this lecture, describing two different problems where the Raoult's law has failed right and that is why the importance of this understanding the system and the utilizing the activity models becomes important. Now, if the vapor phase had been more non ideal then you have to use fugacity coefficient also which of course, I am not covering here which you can you can do that. The rest of the process is similar you have to just make use of the fugacity coefficient using some equation of this ok.

So, with that I will stop and see you in the next lecture.