Aspen Plus Simulation Software- A Basic Course for Beginners

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Lecture - 15
Analysis Tools (Ternary mixtures), Data and Regression (Part 1)

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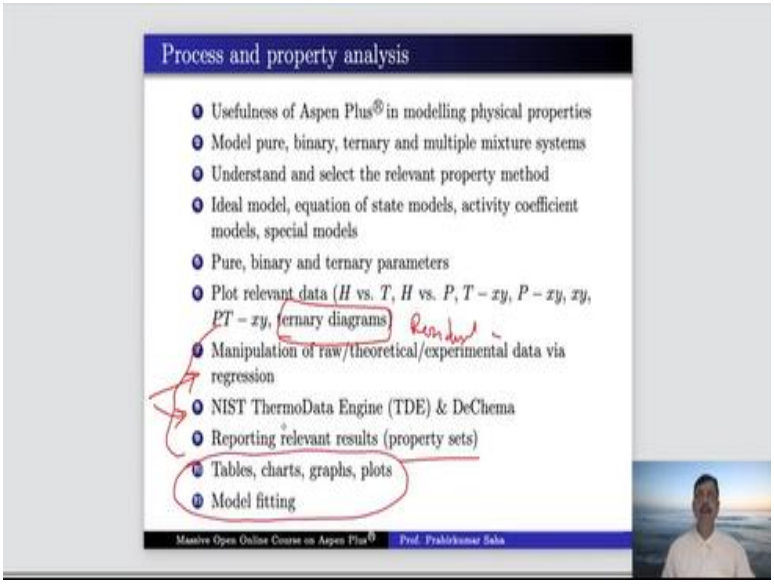

Welcome to the massive open online course on Aspen plus. In today's lecture we shall continue with the last portion of plotting relevant data on ternary diagrams and we will also learn residual curves and then we shall go to the regression of data, collection of data from openly available data banks and reporting relevant results on property sets. So, this is the portion which is actually the last portion of this process and property analysis because this portion we have already discussed in the previous lectures.

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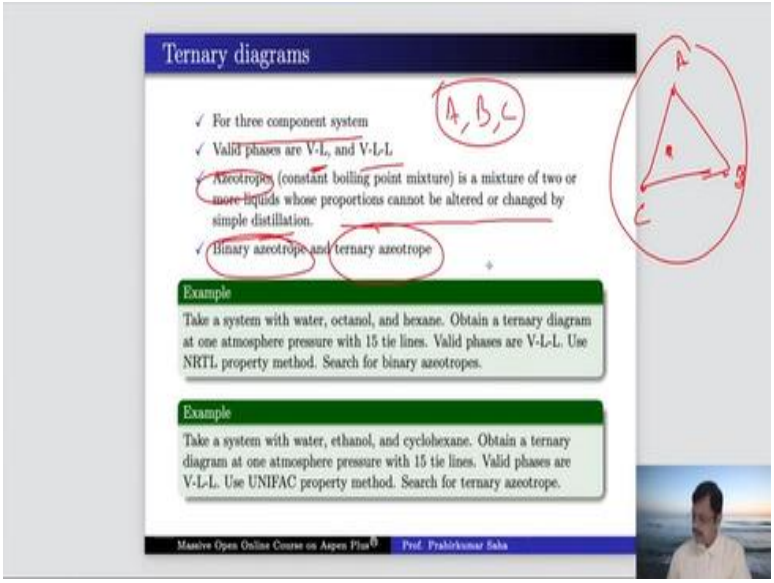

So, first we begin with ternary diagram, as the name suggests it is of three component system, there should be A, B and C. Those who have worked on extraction system you might remember that we have a triangular graph where the corners of the triangular chart have 100% A, 100% B and 100% C. So, any portion of the chart, it indicates a mole fraction of A, mole fraction of B and mole fraction of C.

So, this is called ternary diagram, we can work on valid phases, either it can be vapor liquid or it can be vapor liquid liquid, two liquids two immiscible liquids something like water and organics. Then we can identify the azeotropes, what are the azeotropes? Azeotropes are a mixture of two or more liquids whose proportion cannot be altered or changed by simple distillation. Basically, it is a constant boiling point mixture, where the two components cannot be separated by distillation.

So, there are two types of azeotropes, one is binary azeotrope, another is ternary azeotrope. Binary azeotrope means, when there is a two component mixture which is inseparable and ternary azeotrope, means a point where three component mixture is there and none of them are separable. So, we shall learn about these ternary diagrams with this couple of examples. First, we take the first example, we have three components: water, octanol and hexane.

So, we are asked to obtain a ternary diagram at one atmosphere pressure with 15 tie lines. Valid phases are Vapour-Liquid-Liquid because we have water, we have hexane and they are not miscible that much. We are asked to use the NRTL property method and we have to search binary azeotrope. So, this is our task, the first task; for that let us go to the aspen simulation window.

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So, first let us add the components water, octanol and hexane and the method is NRTL, so choose NRTL method and find out all the binary parameters, temperature dependent binary parameters are there. And the source is for octanol hexane system it is VLE-IG, for water hexane it is LLE-ASPEN and water octanol it is VLE-IG. As water and hexane, they are not miscible, so it is liquid liquid equilibrium, so AIJ AJI, BIJ BJI, all of them are the parameters of the model.

Now we have to bring the ternary diagram. So, let us bring the ternary diagram over here. So, this is the analysis tool, let us bring the ternary diagram. We have water, octanol and hexane. All three components are there, the property method is NRTL and it is one atmosphere pressure. So, we do not have to change anything other than the number of tie lines because we are asked to draw 15 tie lines.

So instead of 5, let us write 15 and we are ready to run the analysis. So, run the analysis, it will take some time, so analysis is done. So, this is the ternary diagram that we were discussing. So, here we have 100% octanol and this is the portion where we have 100% water and at this point, we have 100% hexane. And we have a couple of azeotropes over there, so these are the tie lines we have, 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15. 15 tie lines.

1 to 15 and we have two azeotropes. Now where do we find those azeotropes? One azeotrope is somewhere here you can see, one diamond shaped azeotrope and another azeotrope is hidden somewhere here. Now if you want to know the point at which the azeotrope or what is the mole fraction of components at the azeotrope, you can just go to this azeotrope condition. And you will find it here.

Both the azeotropes are binary because, in both of them the third component has zero mole fraction. So, at 99.5 °C, we have water and octanol azeotrope with no hexane and at 61.43 °C, we have water and hexane azeotrope with no octanol. Now this azeotrope is very well visible in the ternary diagram, here we see 21% of water and 79 % of hexane. So, we just go to this place, you see here, this is 0.21 of water and hexane is 0.79 at this point. And we do not have any octanol over here because the azeotrope lies on this line is the 0% line of octanol. **(Video Ends: 09:24)**

So, this is the first example that we have and we have a second example of a ternary diagram where we have water, ethanol and cyclohexane. Here also we are supposed to obtain the ternary diagram at 1 atmosphere with 15 tie lines. The valid phases are VLL, vapor liquid liquid and we are

supposed to use the UNIFAC property method and there is a ternary azeotrope we have to search for. **(Video Starts: 10:00)**

So, for that let us open a new simulation, we have water, ethanol and cyclohexane. So, let us write water, ethanol and cyclohexane. So, actually we are looking for this particular component, so add the selected component and let us rename it, we write it here CYCLOHEX. Now we are supposed to use the UNIFAC property method, press next and run, so property calculations are done. Now again we bring in the ternary diagram water ethanol cyclohexane UNIFAC property method, we have 15 tie lines, run analysis.

So, we get another ternary diagram, shape and nature is the same but here you find there are four azeotropes; 1 2 3 4. One of them is very clear at point three, the other three are hidden somewhere. Anyway, let us go to the azeotrope concentrations. So, we have four azeotropes, the first, third and fourth these azeotropes are binary azeotropes because in these azeotropes, you have one of the components having zero mole fraction. **(Video Ends: 12:35)** That means that particular component is absent in the mixture.

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They are binary mixtures. But the second azeotrope has all three components; water, ethanol and cyclohexane, it has 15% water, 31% of ethanol and 54% of cyclohexane and that azeotrope is available at 62.39 ℃. So, that is how you can study the ternary diagram and you can map the azeotropes whether it is binary or ternary, you can find out the azeotropes.

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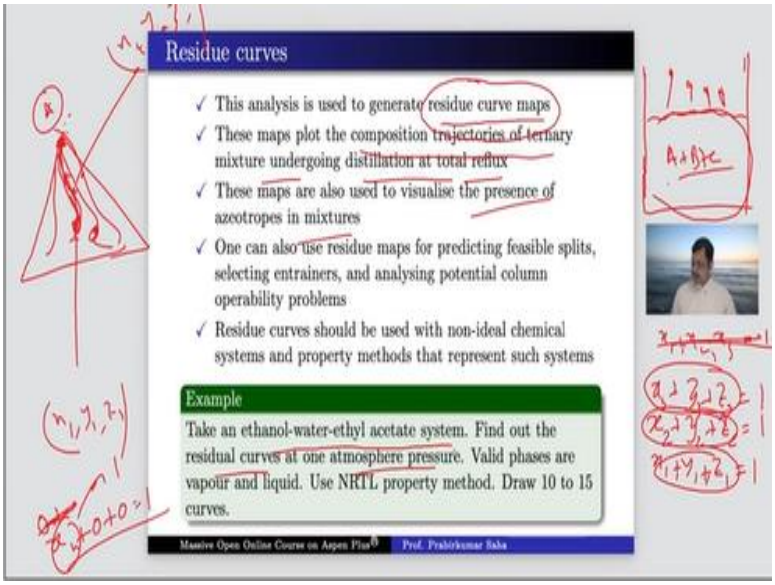

Next, we will learn about the residue curve. Now what is the residue curve? This analysis is used to generate residue curve maps and these maps plot the composition trajectories of ternary mixture undergoing distillation and total reflux condition. Now the question is what is this composition trajectory of ternary mixture? Basically, if you have a container having three components A, B and C is a mixture of three components and it is open.

Then as the time progresses, A, B and C, they evaporate. So, initially the mole fractions of A, B and C will be, say, x_1, y_1 and z_1, total it should be 1. The next moment as the components A, B and C they evaporate they will not evaporate at the same rate because components A, B and C they have different volatilities. So, the more volatile components will evaporate faster than the less volatile components.

And then the next moment the composition will be x_2, y_2 and z_2, then after some time it will be x_3, y_3, z_3 and so on. That means as the time progresses the residual liquid will have these compositions. Now if we plot them, suppose if this is the initial composition which is x_1, y_1 and z_1, the next moment if we plot over here, this may be x_2, y_2 and z_2 and so on. The next composition may be somewhere here, so we can safely plot a trajectory.

So, from the initial condition to the final condition, suppose it will end over here, where it will end? It will end at the lowest volatile component because in the residual curve the last drop of the liquid which will get evaporated must be the least volatile component. If it is A, then the mole fraction of the last component should be $x_n + 0 + 0 = 1$, where x_n is equal to 1. That means this is the pure A that will evaporate at the last.

So, this particular trajectory is called the residue line, residue curve. And if we start from different initial points we will get this curve, this curve, this curve and so on. So, that particular map is called residue curve map and these maps are also used to visualize the presence of azeotrope in the mixture. Now when we will take the example of ethanol water ethyl acetate system and find out its residual curve at one atmosphere pressure, we have valid phases vapor and liquid.

Now here everything is water soluble, both ethanol and ethyl acetate. All of them are soluble in each other. So, we have only one liquid phase, one vapor and one liquid phase. We will use the NRTL property method and we will draw 10 to 15 curves. So, for that let us again go back to our aspen plus window.

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So, you have water, ethanol and ethyl acetate, so water, ethanol and ethyl acetate, find it. We are looking for this particular component. So, add the selected component, let us rename it as ethyl ace, so we are supposed to use the NRTL method. So, place NRTL, run next, binary parameters to be calculated. Now you have to bring in the residue curve. So, bring in the residue curve, we have water ethanol and ethyl acetate at one atmosphere pressure, valid phases are vapor and liquid.

And we are supposed to have 10 to 15 curves, that is what it has been asked for, so run analysis. We have 15 curves; curve 1 curve 2 curve 3 curve 4 and so on. So, this is the residual curve that can be generated from the residual curve method.

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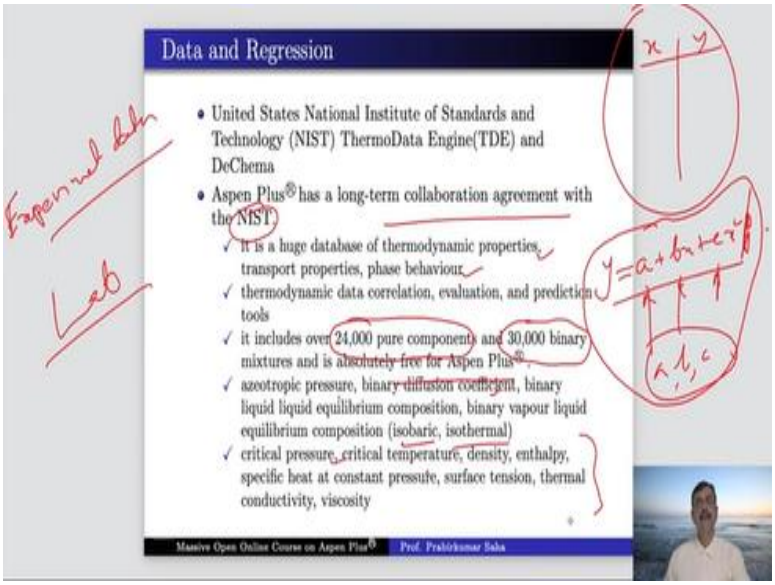

Next, we will learn what data is and how to do the regression. Now you already know what regression is? Suppose if you have a vapor liquid equilibrium data x versus y and if you say your vapor liquid equilibrium model equation is say; $y = a + bx + cx^2$ so on up to cx square, then you have to put the values of x and y data on that and find out the values of a b and c which are the model parameters and this is called the regression.

So, you have to have a data set and you can do the model regression based on that. Now the question is from where you will get the desired data set? Obviously, you can say that it will be obtained from experimental data. So, you can do the lab experiment yourself and gather the data that you can use for regression. But aspen has a long term collaboration agreement with NIST, what is NIST?

It is the United States National Institute of Standards and Technology. So, this NIST has a huge database of thermodynamic properties, transport properties and phase behaviour of a lot of components, may be around 24,000 pure components and around 30,000 binary data mixture and the good news is that, it is absolutely free for aspen plus users, you do not have to pay anything for this data. I will show you how to gather the data from the NIST database.

We will get this data azeotropic pressure, binary diffusion coefficient, binary liquid liquid equilibrium composition, vapor liquid equilibrium composition at isobaric and isothermal condition, the critical temperature and pressure, density, enthalpy and all sort of properties that you can think of are there in NIST database.

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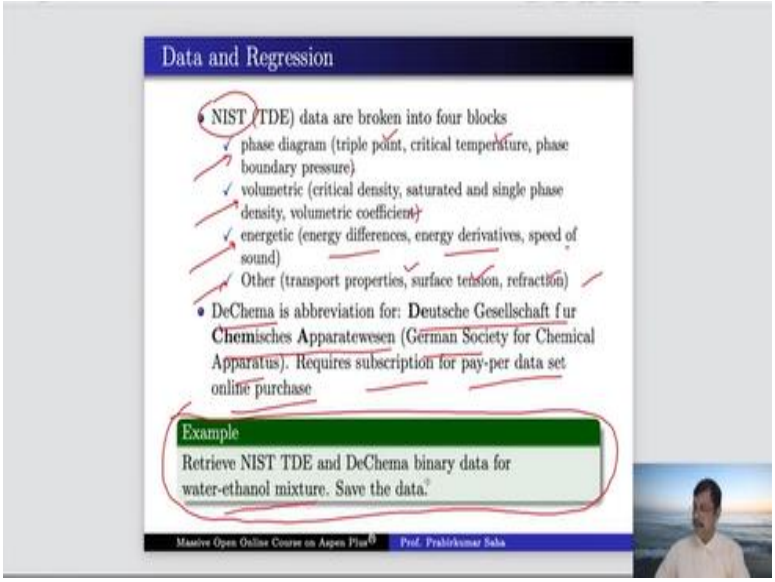

Now in the NIST database, they are broken into four blocks, these are the blocks; phase diagram block, volumetric block, energetic block and other blocks. The name suggests phase diagram block, it will have triple point, critical temperature, phase boundary pressure etcetera. Volumetric block has density, saturated single phase density, volumetric coefficient and energetic block contains energy differences, energy derivatives, speed of sound etcetera.

And other data blocks contain transport properties, surface tension, refraction and so on. So, this is about NIST. Similarly, there is another database which is called DeChema and it is an abbreviation for a German term which loosely translates into English as German society for chemical apparatus. So, it also has a lot of data but the problem is, it requires subscription, you have to pay per data set online purchase not free of cost.

Now I will give you an example of how to retrieve the data from NIST TDE and DeChema binary data for water ethanol mixture and how to save the data. For that, let us go back to our aspen plus simulation window.

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Here you will find the data source NIST, DeChema and DIPPR, so DIPPR is the common data source which you always use. DIPPR comes along with the aspen plus software, but NIST and DeChema should be downloaded online. So, for that you just add NIST, you click NIST, suppose you want binary mixture of water and ethanol, water and ethanol mixture, binary mixture of water and ethanol to retrieve data.

So, it will take some time to retrieve binary experimental data, this may take a few minutes, you have to wait. Well, it didn't take that much of time, anyway we are happy and we get this binary data. So, if you see binary VLE, suppose this is the binary VLE 037, you have so much data, data set, VLE 003 to 320. Now if you say that I want to catch this data and say this data binary VLE 049.

So, here also you can find the temperature versus liquid mole fraction of water and vapor mole fraction of water at this particular pressure. So, the pressure is 101 kPa, and from where this data have been extracted? It has been said by Jones. C. A, so this is the author and source is industrial engineering chemistry 1943 volume 35, so the title of the paper is equilibrium still for miscible liquids data on ethylene dichloride toluene and ethanol water.

So, this is the article from where this data has been extracted. Now suppose you want to save binary VLE data 037 which has been taken at pressure 66.661.2 Pascal. So, here you have to say save data and here you have to choose VLE 37 and VLE 49, so press OK. So, the moment I press OK, here you will have the data set saved over here, so press OK. Here two data banks have been opened; the first one is water ethanol, these are the data, so this is the data set.

And for the second data set we have the similar data set, obviously it is at different pressures, anyway let us try to find out the xy diagram, for that this is y versus x. So, we have water ethanol mole fraction, so this is the vapor liquid equilibrium curve and this has been obtained from this data set. Now let us take this one, the second data set. Here also we can generate one plot. So, here also we got another plot of water ethanol.

Now we have two plots, now we want to compare them, we want to see whether these two plots match with each other. Let us try, for that we will merge the plots, do it with a single y axis, now you can see it has merged. So, here we have the data for both the experimental data set and all of them that come within this line, so that visually gives us confidence that both the data sets have reliable data.

Because one data set has been obtained from a paper in 1943 and another data set has been obtained from somewhere else and both of them have a similar kind of data structure. So, we can rely on this data set, so this is how we bring in the NIST data. Similarly, we can go for DeChema binary data, for that we have to click on DeChema. And we do not select this one, we select only water ethanol and vapor liquid equilibrium of the mixture.

So, I searched for DeChema Dethem on the web. So, it will open the Dethem on the web, so aspen has its own web browser where it will search, so just increase it. Now you can see that we have isobaric vapor liquid equilibrium data, both isobaric and isothermal for the system ethanol on water published in different years within this temperature range and pressure and so many lines, what does it mean? Lines means each and every line has a pair of data.

So, eight lines means we have eight pairs of xy data, for 71 lines means we have 71 pairs of xy data and you can understand that as the number of data points increases the price also increases. So, for six points or eight points we have only 59.5 euro we have to pay, whereas for a higher amount of data we have to pay 142.8 euro. So, in order to purchase you have to first register yourself and login and then you have to select, suppose you select this one and check out.

So, it says one item is there in the cart, you may say order, so here you have to log into your system. Once you do it you will be given the option to pay, you have to use your credit card and you can pay and get the data.

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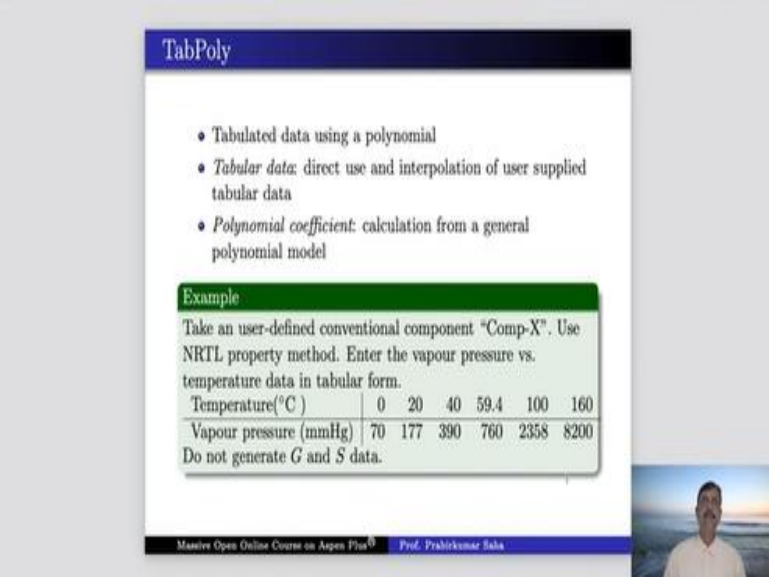

Now we have something called Tab Poly, as the name suggests tab poly means it is tabulated data using a polynomial. So, either polynomial or tabulated data, actually when you have a user defined conventional component which is not available in the aspen database, then you can enter certain data and you can set a characteristic of that particular component in your database. For instance, suppose you have a user defined conventional component called Comp X.

The name suggests that this component is not within your aspen database. So, you are giving it a name Comp X, so how to use or tab poly for that. So let us go to the simulation window once again.

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Let us user define Comp X, so this is our component id, we press finish. So, it does not have any component name, obviously it does not have analysis also, let us not bother about that because we have to give certain data to it. So, there are some characteristics that can be obtained. For that you have to go to the method and click tap poly and here create a new id for tab poly and the property you can choose over here.

What kind of property that you want to feed into this Comp X? For instance, we have vapour pressure versus temperature data in tabular form. So, we want to feed this data, we have several options but we will choose vapour pressure data because we do have this data to feed in. Now we have to set a property method, let us choose a property method, first it is NRTL property method NRTL, so choose the property method NRTL.

Here also we have few options for data generation. Data generation from user input enthalpy or heat capacity data. So, you can generate Gibbs free energy data or you can generate entropy data or you can generate both or you may not be willing to generate any data. For timing, let us not complicate the matter and do not generate anything. So, go to data. So, here you have to set the component first. So, we have Comp X, so we have to give the vapor pressure data for this component x.

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We can give it in tabular form or in polynomial form.

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Polynomial form means it will have $y = a_1 + a_2x^2 + a_3x^3 + \ldots + a_8x^8$. So, this is the polynomial model, we have the minimum and maximum temperature for this model is also given. But we do not have a polynomial coefficient, so instead we will give tabular data and once we give the tabular data, aspen can calculate the polynomial or it can extrapolate.

So, let us go and check the data, we have temperatures at 0, 20, 40, 59.4, 100, 160. So, the temperatures are 0, 20, 40, 59.4, 100 and 160. Similarly, the values of vapor pressure we have are 70 177 so it is 70, 177, 390, 760, 2358 and 8200. So, we have the vapor pressure data that we have fed into the identity of Comp X, so from there aspen can estimate for Comp X. Now similarly, if you have some other data.

For instance, if you have the data of say surface tension or vapor thermal conductivity or you may have data of liquid viscosity. In such a situation you can again go to tab poly and create, say liquid viscosity, choose liquid viscosity for NRTL method, in the data set. You choose Comp X tabular data. Now at various temperatures you can give the values of liquid viscosity. So, like that you can add the tabulated data or polynomial coefficient for Comp X as much data you can give.

So, more and more data you give aspen will have less effort and more accuracy in characterizing the unknown component that you have defined.

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