Aspen Plus Simulation Software- a Basic Course for Beginners
Prof. Prabirkumar Saha
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture - 14
Analysis Tools (Pure Components and Binary Mixtures)

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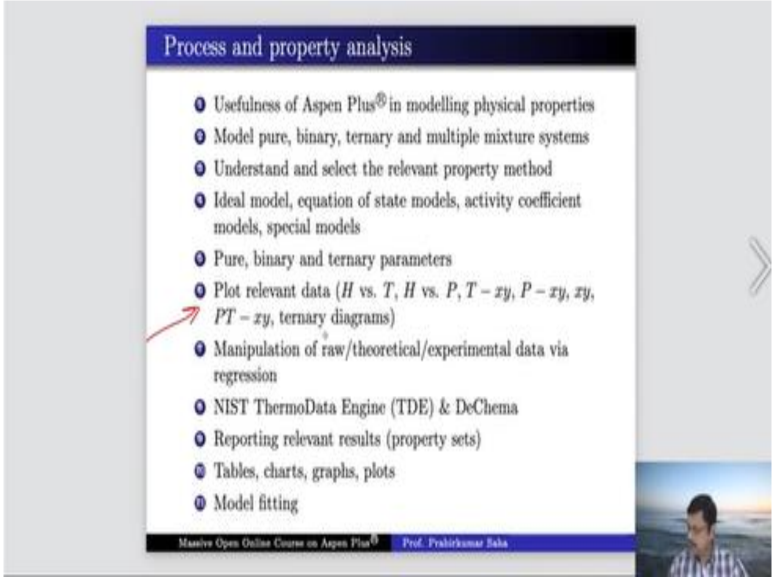

Process and property analysis

- Usefulness of Aspen Plus® in modelling physical properties
- Model pure, binary, ternary and multiple mixture systems
- Understand and select the relevant property method
- Ideal model, equation of state models, activity coefficient models, special models
- Pure, binary and ternary parameters
- Plot relevant data (H vs. T, H vs. P, $T-xy$, $P-xy$, xy, $PT-xy$, ternary diagrams)
- Manipulation of raw/theoretical/experimental data via regression
- NIST ThermoData Engine (TDE) & DeChema
- Reporting relevant results (property sets)
- Tables, charts, graphs, plots
- Model fitting

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Welcome to the massive open online course on aspen plus. This is the fifth week. In this week we are continuing with the lecture series on process and property analysis. We will learn these two topics in today's lecture. One is plotting of relevant data, enthalpy versus temperature, enthalpy versus pressure; temperature versus xy pressure versus xy, xy means the mole fractions of any component in vapour phase and liquid phase, xy, P, T xy and ternary diagrams. And reporting of relevant results in tables charts graphs and plots.

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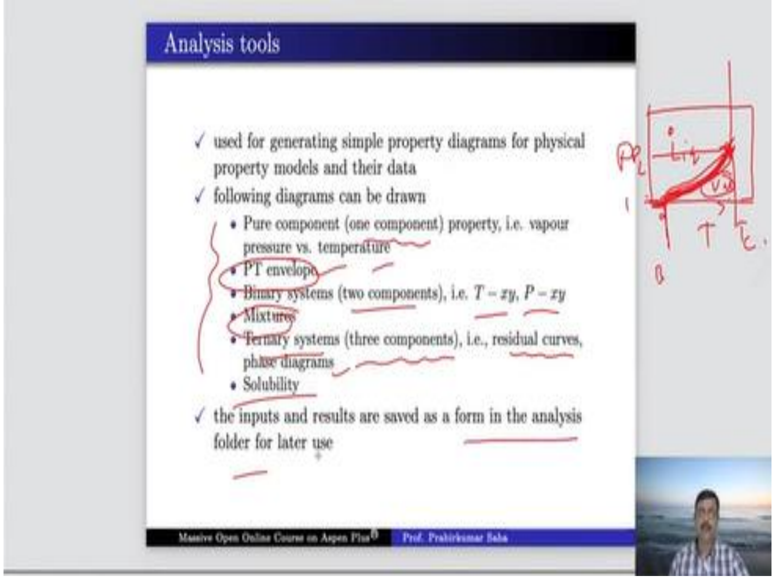

Analysis tools

- ✓ used for generating simple property diagrams for physical property models and their data
- ✓ following diagrams can be drawn
  - Pure component (one component) property, i.e. vapour pressure vs. temperature
  - PT envelope
  - Binary systems (two components), i.e. $T-xy$, $P-xy$
  - Mixtures
  - Ternary systems (three components), i.e., residual curves, phase diagrams
  - Solubility
- ✓ the inputs and results are saved as a form in the analysis folder for later use

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So, let us begin with the analysis tool through which we can develop this T xy, P xy diagram etcetera. The analysis tools are used for generating simple property diagrams for physical property models and their data. And the following diagrams can be drawn one is pure component property vapour pressure versus temperature that means only one component. Then PT envelope, PT envelope means it will be something like this where this will be P and this will be T.

And this will be liquid phase and this will be vapour phase will get a line and this is the boiling point line because as the temperature goes higher with low pressure it will be vapour phase and with low pressure low temperature and high pressure it will be liquid phase. So, this is the boiling point line and we will have the minimum over here. This is the boiling point at one atmosphere and we will have a critical point.

So, the graph will end somewhere at the critical point which will be critical pressure and critical temperature. So, this is called PT envelope. And then for binary systems that are two component we will have T xy diagram and P xy diagram. Then we will discuss about mixtures ternary systems like three components. We will learn residual curves and phase diagram and finally we will learn about solubility.

And then we will also learn the inputs and results that could be saved in the form of analysis folder for later use.

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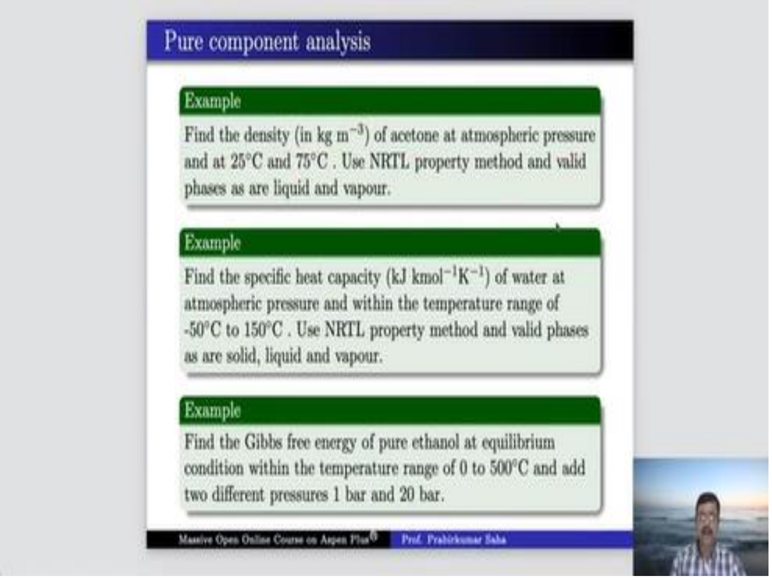

Pure component analysis

Example

Find the density (in kg m^{-3}) of acetone at atmospheric pressure and at 25°C and 75°C . Use NRTL property method and valid phases as are liquid and vapour.

Example

Find the specific heat capacity (kJ $kmol^{-1}K^{-1}$) of water at atmospheric pressure and within the temperature range of -50°C to 150°C . Use NRTL property method and valid phases as are solid, liquid and vapour.

Example

Find the Gibbs free energy of pure ethanol at equilibrium condition within the temperature range of 0 to 500°C and add two different pressures 1 bar and 20 bar.

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Now this can be better learned through some examples. The first example that we have it is about finding the density of acetone at atmospheric pressure at two temperatures, one is 25 ^{0}C another is 75 ^{0}C. We can take the property method which is NRTL property method and valid phases are liquid and vapour. We have to go to the aspen plus simulation window.

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So, let us press acetone over here and we have to select a property method. Let us choose NRTL and then run that is pure component analysis. So, we have to bring in the pure component over here. So, this is the pure analysis. So, if you click, so there are various property methods like thermodynamic, transport or all. So, we chance choose thermodynamic property method and they have asked us to find out the density which is given by RHO.

So, RHO is the density of a pure component. So, choose RHO in kg/m3, valid phases are vapour and liquid. Now we have available component acetone only. So, just select acetone pressure is one atmosphere and we can give the list of temperatures. Temperature can be given in the range 0 to 100 ^{0}C with a 50 interval or 20 interval or 10 interval as per your choice or you can give in logarithmic or list of values. So, we have two temperatures over here.

25 ^{0}C and 75 ^{0}C. So, we give list of values. So, let us write 25 ^{0}C and 75 ^{0}C. Now we have to run analysis, press it. So, it is running and the results are available. So, you can see the green line is liquid RHO acetone that is the liquid acetone density which is around 786 kg/m3 at 25 ^{0}C and it is 725 kg/m3 at 75 ^{0}C. So, this is liquid density.

Now this vapour density curve the blue one is not of any relevance. Because you know that at atmospheric pressure and at 25 ^{0}C acetone is liquid. But just because you have given two phases that is vapour and liquid it has given some result. So, in this case we disregard the vapour row acetone. Because acetone is not in vapour phase at this moment.

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So, let us go to the next example. Here they have asked us to find specific heat in kJ/kg K of water at atmospheric pressure and within the temperature range of (minus) - 50 ^{0}C to 150 ^{0}C. We know at atmospheric pressure water is solid in ice form from (minus) - 50 ^{0}C to 0 ^{0}C and then from 0 ^{0}C to 100 ^{0}C, it is water liquid water and above 100 ^{0}C it is vapour. So, all three stages are available here. Here also use NRTL property method and as expected valid phases are solid liquid and vapour.

(Video Starts: 08:10)

Go back to our aspen window. In specification add water, press next; run. Now let us again bring in pure analysis. Here you have to choose water not acetone and specific heat constant pressure heat capacity of a pure component in kilojoule per kilo mole k and valid phases are vapour liquid and solid, all. And we have (minus) - 52 plus 150 this is the temperature range and let us take number of intervals 50. So, there will be 200 by 50.

So, every 4 ^{0}C we will get one data point. Pressure is 1 atmosphere keep it like this and run analysis. So, you can see here as we have discussed just few minutes back. Up to this point this is ice, solid water and above 100 ^{0}C this one is vapour phase and this is liquid phase of water, this entire thing. So, the green line is liquid CP. So, this portion is relevant for this curve, this portion is not relevant, this portion is not relevant because at one atmosphere the water is not in solid phase.

So, this portion is not relevant at all so as this. What about the red line? It is solid. So, this portion is relevant, not this portion. And finally, vapour CP water it is blue line. So, this portion is relevant, not this one. So, that is how you analyse the specific heat of water at various phases.

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And the next example is of finding Gibbs free energy of pure ethanol at equilibrium condition within the temperature range of 0 to 500 ^{0}C and two different pressures 1 bar and 20 bar.

(Video Starts: 11:29)

So, go back to your specifications, add ethanol over here. They have not asked us to use any property method. Let us keep NRTL only, run. Now let us again choose pure, here, it is Gibbs free energy. So, this is one Gibbs free energy of a pure component ethanol, unit is kilojoule per kilo mole let us say. And at two different pressures 1 bar and 20 bar keep the temperature range from 0 to 500. So, keep it 0 and here 500, first let us say at 1 bar, run analysis.

So, this is the G versus temperature and if the same thing if you do at 20 bar you will get this curve. Now you can always plot these two graphs in the same one. So, for that you have to add in the pure once again. So, bring in pure once again and bring in G, ethanol 500 and this is 1 bar. So, for pure three we have already taken for 20 bar and we run the analysis once again. So, this is the plot. Let us change the legend it is for 1 bar and this one is for 20 bar.

Now we merge these two plots, merge it with G plot. So, you can see two plots are merged. Let us move the legend over here. Here you can see the blue line is this one that is for 1 bar and this is for 20 bar. The green line is true for 20 bar. But do not think that they are almost superimposing each other because the y axis are at different scale although their temperature scale is same 0 to 500. Now we can compare it better way by merging the y axis.

So, for that we have to do we have to press y axis map and press single axis and press ok. Now it is better. So, we have single axis and you can see at any particular temperature say 250 ^{0}C, the Gibbs free energy of ethanol at 20 bar is (minus) - 105000 Cal/mole. So, you can change that unit also instead of Cal/mole you can use joules/kmole or something like that anyway. So, this curve is higher than this. So, this is the type of analysis that you can do.

And you can compare your theoretical knowledge of Gibbs free energy with the result that you get.

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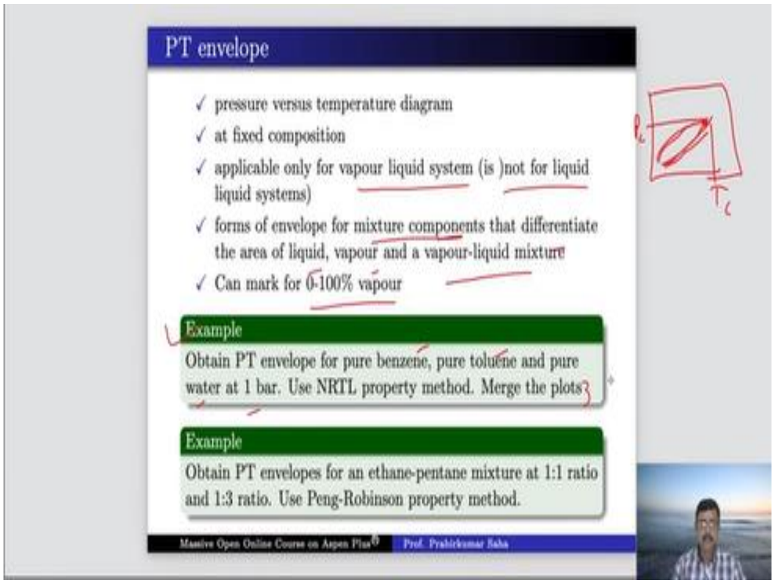

PT envelope

- ✓ pressure versus temperature diagram
- ✓ at fixed composition
- ✓ applicable only for vapour liquid system (is)not for liquid liquid systems)
- ✓ forms of envelope for mixture components that differentiate the area of liquid, vapour and a vapour-liquid mixture
- ✓ Can mark for 0-100% vapour

Example

Obtain PT envelope for pure benzene, pure toluene and pure water at 1 bar. Use NRTL property method. Merge the plots

Example

Obtain PT envelopes for an ethane-pentane mixture at 1:1 ratio and 1:3 ratio. Use Peng-Robinson property method.

The next one we will learn what is PT envelope. Now as I said PT envelope is a pressure versus temperature diagram. So, it is applicable only for vapour-liquid system not for liquid-liquid system and it forms an envelope for mixture compound. For pure component it is something like this because it tries to find out the critical pressure and critical temperature point. But for mixture it creates a kind of envelope where you will have a dew point line and a bubble point line.

So, that actually differentiates the area of liquid vapour and vapour liquid mixture. It can mark for 0 to 100% vapour. So, to understand it better let us take this example first. So, it says obtain a PT envelope for pure benzene, pure toluene and pure water at 1 bar. Use NRTL property method merge the plots. So, let us try this. For that let us go back to aspen simulation window and look for benzene toluene and water. Water is already there in our specification.

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So, let us add benzene and toluene. So, press next, run. Now you can call PT envelope. So, here for benzene just gives 1 kilo mole per hour, do not give anything else, because you are looking for pure benzene. So, you have a flow of benzene only benzene nothing else and pressure it should be one bar. So, let us say one bar pressure and then run analysis. So, you can understand that at one atmosphere pressure boiling point of benzene at one atmosphere is 79 or 79.5 ^{0}C.

Whereas the critical temperature of benzene is 287 ^{0}C and critical pressure is 47.8. So, let us write it for benzene. Now let us bring the second PT envelope, it is for toluene. So, just give 1 kilo mole per hour it does not matter you can give 10 kmole/hr also or any number you want. Just you have to mention that it is a pure liquid that means only one of them is going in not others. Here also you press 1 bar and run analysis.

So, here also you can find that at one atmosphere the boiling point of toluene is around 110 ^{0}C. Whereas the; critical temperature and pressure of toluene is 318 ^{0}C and 40.7 bar. Just change it to toluene and bring in the PT envelope once again. And this time you have to choose water at 1 bar, run analysis. Now water is very common liquid and you know what is the boiling point of water at 1 atmosphere, it is 99.6.
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It says 99.6 because it is not 100. Why? Because we; have measured it at 1 bar not 1.01625. Because actually 1 atmosphere pressure is 1.01625. But we have measured at 1 bar. So, the boiling point of water here it is showing 99.6.

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Anyway, we can see what is the critical pressure and critical temperature and you can see it is 373 ^{0}C and 217 bar that is the critical pressure. So, let us change it to water.

(Video Ends: 23:36)
So, we have got PT envelope for pure benzene, pure toluene and pure water at 1 bar using NRTL method. Now they are asking us to merge the plot. So, as to compare the PT envelopes of three liquids that we have got.

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So, for that let us merge plot. So, merge plot with PT envelope 2 and then with PT envelope 1. Now everywhere they have taken a separate y axis for themselves. Now we want to merge them all. So, go to y axis map make it single axis and press ok. So, this is water and one of them will be benzene, I believe this is benzene. So, this is benzene curve this is toluene curve. So, benzene is blue. So, you can compare the PT envelope curve of these three components benzene, toluene and water.

The critical temperature and critical pressure of benzene is this one, this is for toluene and this is for water. And the boiling point at 1 atmosphere are also given, this is for water, this is for benzene and this is for toluene.

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So, that is how you get the PT envelope for three your components.

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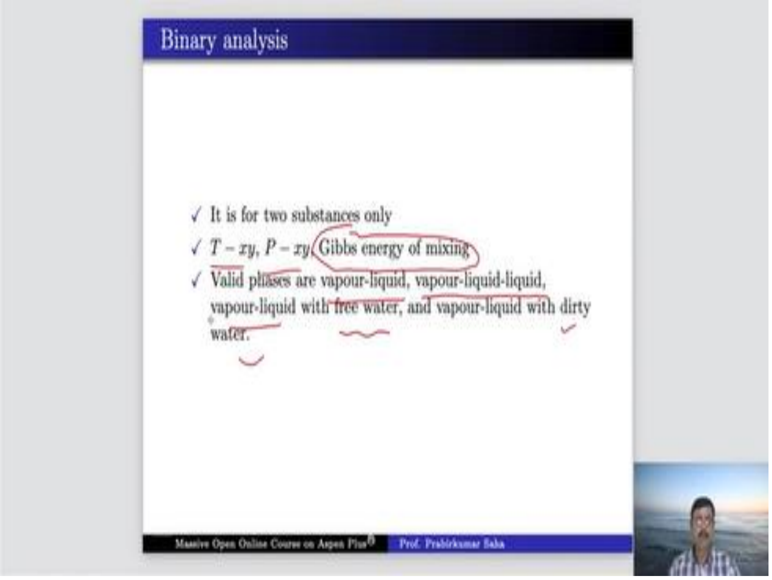

Binary analysis

- ✓ It is for two substances only
- ✓ $T - xy$, $P - xy$, Gibbs energy of mixing
- ✓ Valid phases are vapour-liquid, vapour-liquid-liquid, vapour-liquid with free water, and vapour-liquid with dirty water.

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Now the next one we will learn binary analysis. Now the name suggests it is for only two substances or two components. And we can find out the T xy diagram and P xy diagram also we can see the Gibbs energy of mixing. The valid phases we will have in binary analysis vapour-liquid or vapour-liquid-liquid also vapour-liquid with either free water or dirty water. So, many valid phases are possible for binary analysis.

Now in the second example is asking for PT envelopes for ethane pentane mixture at 1 is to 1 ratio and 1 is to 3 ratio using Peng Robinson property method. So, we have to bring in ethane and pentane over here and take a mixture of 1 is to 1.

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So, let us go back to specification none of ethane and pentane are there. So, we have to add in both of them. So, ethane and pentane, now we have to choose Peng Robinson property method, press next. Now again you bring in PT envelop. And here you have to give 1 is to 1 ratio ethane and pentane and it is not the pressure is not given, but we can take 1 atmosphere. Let us take one atmosphere. So, you can run analysis, here you can see, there are two items.

One is pentane and another is ethane. Now this line this green line is vapour fraction 0 that means it is completely liquid line and this blue line is vapour fraction 1 so it is a completely vapour line. So, this is actually the dew point line and this is the bubble point line. So, in terms of vapour liquid mixture we can argue that this entire area over here, this entire area this is liquid and this entire area this side it is vapour and in between we have vapour liquid mixture.

So, this is the perfect envelope we have where we have one bubble point line and one dew point line like this and this.

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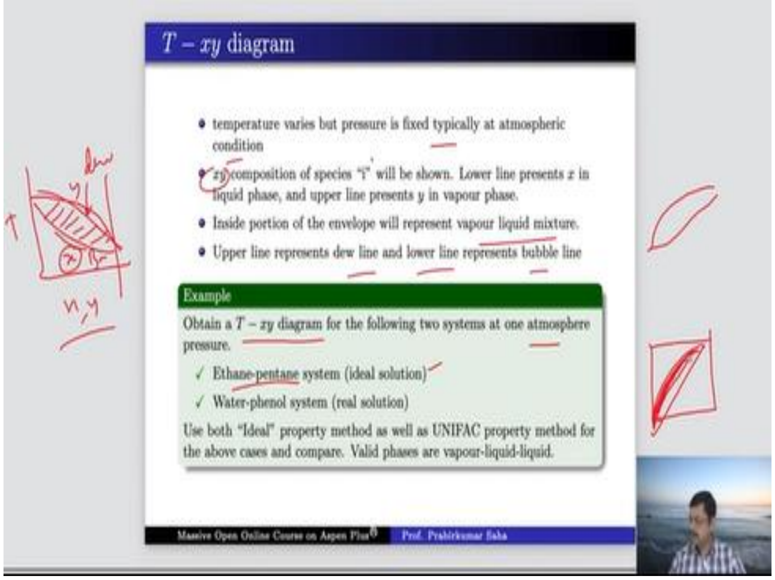

$T - xy$ diagram

- temperature varies but pressure is fixed typically at atmospheric condition
- xy composition of species "i" will be shown. Lower line presents x in liquid phase, and upper line presents y in vapour phase.
- Inside portion of the envelope will represent vapour liquid mixture.
- Upper line represents dew line and lower line represents bubble line

Example

Obtain a $T - xy$ diagram for the following two systems at one atmosphere pressure.

- ✓ Ethane-pentane system (ideal solution)
- ✓ Water-phenol system (real solution)

Use both "Ideal" property method as well as UNIFAC property method for the above cases and compare. Valid phases are vapour-liquid-liquid.

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Now first we will learn T xy diagram. Now this T xy diagram here the temperature varies but the pressure is fixed so, this will represent the x that is the mole fraction of component in liquid phase and this is mole fraction of component in vapour phase. So, this will be the dew point line and this is the bubble point line. So, this T xy diagram will have and the inside portion of the envelope will represent the vapour liquid mixture.

So, this is the portion it will be vapour liquid mixture and the upper line dew line and bubble line we have already discussed. Now let us go to this example. Obtain a T xy diagram for the following two systems at 1 atmosphere pressure; one is ethane pentane system which is an ideal solution. Because ethane pentane system if you see the vapour liquid equilibrium the vary diagram the experimental result and the ideal model simulation result will almost merge.

So, it is an ideal solution. Ethane and pentane they do not have much molecular interaction. Whereas water phenol system it is a real solution. Here they have said that use both ideal property method as well as UNIFAC property method for the above cases and compare. And obviously the valid phases are vapour liquid-liquid. Now water phenol system will have vapour- liquid-liquid because water and phenol they are not they do not mix much. So, let us go back to simulation window.

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Here we have to take ideal process. So, ideal property method and binary diagram with ethane and pentane. So, choose ethane, pentane and starting point of mole fraction of ethane is 0 end point is 1, number of intervals 50 and obviously it is 1 atmosphere at 1 atmosphere so one bar and you can run the analysis. So, this is the ideal case. Now the same thing we can try with UNIFAC model. For that we have to bring in UNIFAC property method and run it.

Then go to the binary method and ethane pentane. The calculation option it will be UNIFAC valid phases vapour liquid-liquid, run analysis. So, this is the second one, ethane and pentane. Now let us change this thing with UNIFAC. So, that we; can differentiate with ideal gas when we merge the graph. Now merge the graphs. So, merging plot with binary this one, merge the axis also.

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So, you can understand for ethane pentane binary mixture whether you take ideal model or UNIFAC model. Their T xy diagrams almost match with each other. Now let us take water phenol system instead. So, this is water we do not have phenol over here. So, let us go to components and add phenol and then next run. Go to binary, take phenol over here and water over here, mole fraction from 0 to 1 water calculation option UNIFAC. So, run analysis, this is UNIFAC.

Now same thing if you want to do with ideal system then check what happens. So, this is the ideal case it has overwritten. So, we do not have the previous one. Let us bring in the second one. So, choose phenol, choose water and calculation option UNIFAC, run analysis. Let us open, rename it UNIFAC and then merge the plot with binary plot three. So, this pair is uniform UNIFAC, red and magenta colour once edit y axis merge them.

Here you can see although the dew point lines of both UNIFAC and ideal cases are somewhat similar. But the bubble point lines are far apart.

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So, it is understandable because water phenol system is not an ideal system, it is a real solution. So, we have to use activity coefficient model not an ideal model.

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So, that is how we generate T xy diagram.

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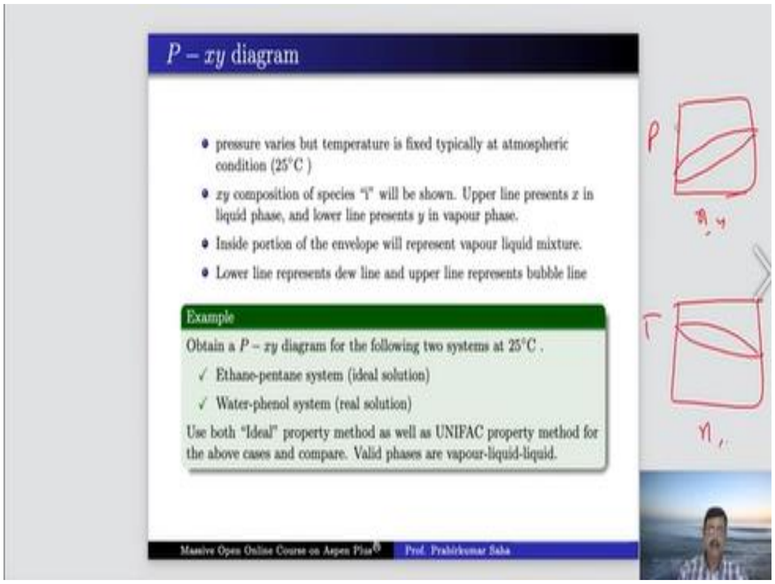

$P - xy$ diagram

- pressure varies but temperature is fixed typically at atmospheric condition (25°C)
- xy composition of species "i" will be shown. Upper line presents x in liquid phase, and lower line presents y in vapour phase.
- Inside portion of the envelope will represent vapour liquid mixture.
- Lower line represents dew line and upper line represents bubble line

Example

Obtain a $P - xy$ diagram for the following two systems at 25°C .

- ✓ Ethane-pentane system (ideal solution)
- ✓ Water-phenol system (real solution)

Use both "Ideal" property method as well as UNIFAC property method for the above cases and compare. Valid phases are vapour-liquid-liquid.

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Similarly, P xy diagram can also be found out. Here the pressure varies but temperature is fixed typically at atmospheric condition that is 25 ^{0}C. Here also the xy composition of species, I will be shown and because it is a P xy diagram. So, upper line will present x as well as bubble line and lower line will present y vapour phase as well as in dew line and the inside portion of the envelope will present the vapour liquid mixture.

And actually, this line this figure will be something like this will be your P x y diagram. Unlike T xy diagram which was something like this, it will be something like this. So, let us solve this problem obtain P xy diagram for the following two systems at 25 ^{0}C. So, our systems are same, the methods are same. We will do only one of them and the rest you can practice yourself.

(Video Starts: 42:29)

So, for that instead of T xy diagram we will have P xy diagram for water phenol, calculation option UNIFAC, run analysis. So, you can understand what it is? It is at 25 ^{0}C, this is the bubble line and this is the dew line. This is x actually it is x y this curve, this axis is xy axis liquid vapour mole fraction of water. And visibly this is a liquid portion this is vapour portion and inside it is liquid first vapour mixture. So, this is how you can get a P xy diagram.

(Video Ends: 43:41)

So, you can practice the other ones I have done P xy diagram at 25 ^{0}C for water phenol system using UNIFAC. So, you can try out with ideal property method and also you can change the components to ethane and pentane and try out both ideal property as well as UNIFAC property, others will remain same.

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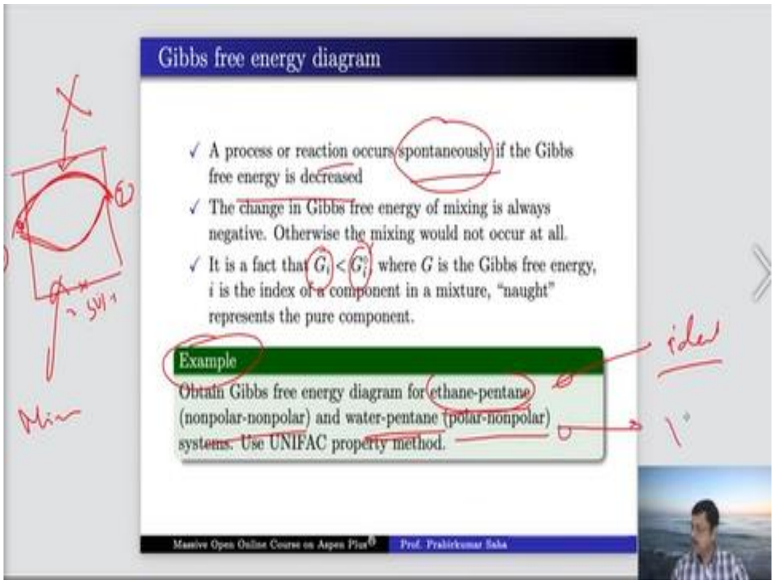

Gibbs free energy diagram

- ✓ A process or reaction occurs spontaneously if the Gibbs free energy is decreased
- ✓ The change in Gibbs free energy of mixing is always negative. Otherwise the mixing would not occur at all.
- ✓ It is a fact that $G_i < G_i^\circ$, where G is the Gibbs free energy, i is the index of a component in a mixture, "naught" represents the pure component.

Example

Obtain Gibbs free energy diagram for ethane-pentane (nonpolar-nonpolar) and water-pentane (polar-nonpolar) systems. Use UNIFAC property method.

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Now let us learn Gibbs free energy diagram. Now as you understand that gives free energy for a process or reaction if the Gibbs free energy is decreased then only the spontaneity of that reaction or mixing that will be established. Suppose the Gibbs free energy of a pure component i is Gi 0 and the Gibbs free energy of the same component i in a mixture is Gi then Gi has to be less than Gi naught in case of a spontaneous process or a reaction.

So, suppose it is a binary mixture then this is the Gibbs free energy of component 1 and so this is the Gibbs free energy of component 2. If it is a 50-50 mixture then Gibbs free energy should look like this. Then only the system is spontaneous or the mixing is spontaneous. If the Gibbs free energy diagram is something like this then it is not a spontaneous reaction or we can conclude that these two components are not miscible at all.

Now we shall learn this Gibbs free energy diagram through this example where they have asked us to obtain a Gibbs free energy diagram for ethane pentane and water pentane systems. As we know ethane pentane is a non polar non polar type of system so it is an ideal system, it can mix. Whereas water pentane system is polar non polar so it is not miscible at all. You can use UNIFAC property method for running this. So, let us again go back to our simulation.

(Video Starts: 46:24)

So, here bring in binary, bring in Gibb's energy of mixing, ethane, pentane, calculation option UNIFAC at 1 bar pressure temperature is 25 ^{0}C. So, run the analysis here. You can see at 25 ^{0}C and one atmosphere pressure the Gibbs free energy of mixing it is something like this. So, Gibbs free energy of the mixture is lower than the pure components. So, we can conclude that this particular pentane and ethane mixture is a spontaneous mixing component, they will mix spontaneously.

Now let us bring in another one which is water pentane. So, water and pentane other conditions remain same. Let us run the analysis. So, here you can see the Gibbs free energy is increasing for water pentane system. That means this mixing is not spontaneous at all, this system is not spontaneous.

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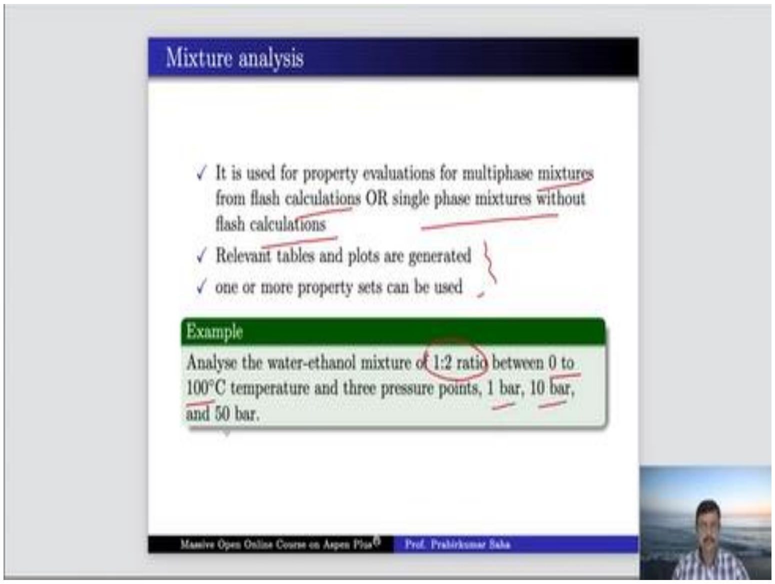

Mixture analysis

- ✓ It is used for property evaluations for multiphase mixtures from flash calculations OR single phase mixtures without flash calculations
- ✓ Relevant tables and plots are generated
- ✓ one or more property sets can be used

Example

Analyse the water-ethanol mixture of 1:2 ratio between 0 to 100°C temperature and three pressure points, 1 bar, 10 bar, and 50 bar.

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Now we will learn the mixture analysis. Now the mixture analysis is used for property evaluations of multiphase mixtures from flash calculation or single-phase mixtures without flash calculations.

The relevant tables and plots are generated and one or more properties can be used. Now let us take this example, analyse the water and ethanol mixture of 1 is to 2 ratios between 0-to-100-^{0}C temperature and 3 pressure points that is 1 bar 10 bar and 50 bar. So, let us take this mixer analysis. Now before that you need to prepare a property set.

(Video Starts: 49:58)
In the previous lecture we learned how to set a property set. So, let us enter the ID PS 1 and let us say we want CPMX. So, this is the heat capacity CP of a mixture and we can ask for mu MX. So, that is the viscosity of a mixture and Gibbs free energy of a mixture. So, the unit we can choose as centipoise this one as kilojoule per kilo mole k and GMX we can choose say kilojoule per kilo mole. And the qualifier let us say the vapour and also you can say liquid also no problem if we have a liquid phase that is not a problem.

So, we have set the property. Now let us take mixture analysis, choose mixture. What are the components? Components are water and ethanol. So, bring in water and ethanol in 1 is to 2 ratios. So, let us say this is 1 and this is 2 so this is 1 is to 2 ratios. And the temperature ranges from 0 to 100 ^{0}C with 20 number of intervals and pressure 1 bar, 10 bar and 50 bar. So, enter the values 1 bar, 10 bar and 50 bar so for 3 values we get. And what are the properties to report?

We have already said there just select them and run analysis. So, this is the mixture diagram we get. Let us say one by one this line all the lines are almost super imposed. So, it is very difficult to distinguish between them. But we can definitely look for this one, this one should be I think liquid GMX at 50 bar. So, this curve is liquid GMX for 50 bar and its y axis values are given how with temperature increase it changes its value.

So, these are graphical representation of all the properties from this temperature point to that temperature point at various pressure. So, that is how you can get the mixture properties.

(Video Ends: 54:10)
So, we end our lecture at this point. We will continue in the next lecture. Thank you.