Upstream LNG Technology
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Lecture – 30
Equilibrium in multicomponent systems

Welcome. After learning about the binary systems, today we shall be analyzing some of the multi component systems now; this lecture pertains to the equilibrium in multi component systems

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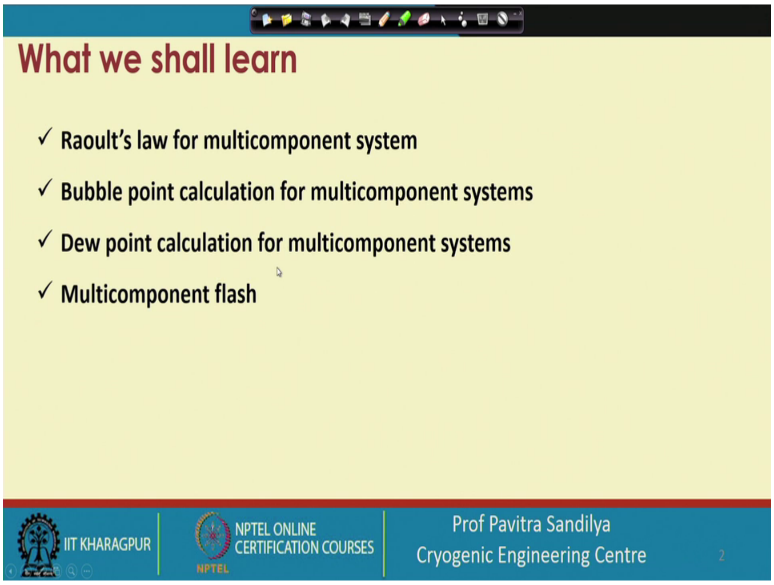

What we shall learn

- ✓ Raoult's law for multicomponent system
- ✓ Bubble point calculation for multicomponent systems
- ✓ Dew point calculation for multicomponent systems
- ✓ Multicomponent flash

In this particular lecture, we shall be learning about the Raoult's law, how it is applied to the multi component systems, then bubble point calculation dew point calculation for a multi component systems and multi component flash, we learnt these things already for the binary systems and there will be some modifications, when we are considering the multi component systems.

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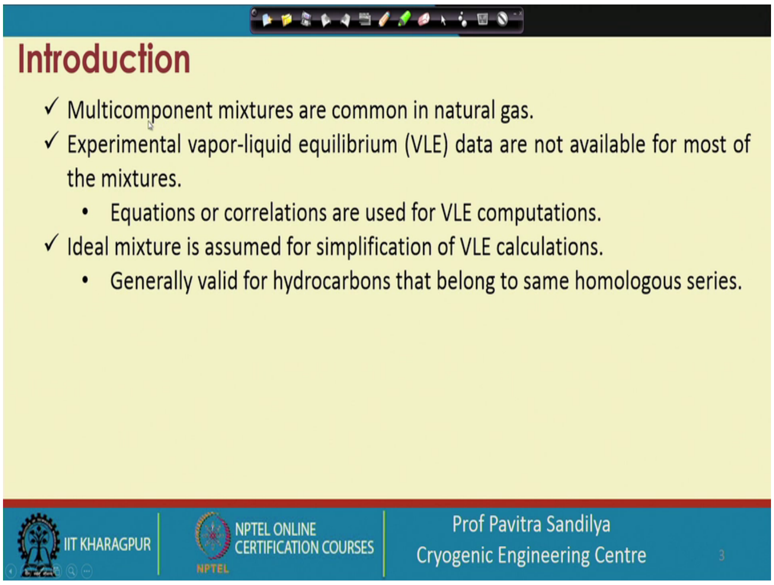

Introduction

- ✓ Multicomponent mixtures are common in natural gas.
- ✓ Experimental vapor-liquid equilibrium (VLE) data are not available for most of the mixtures.
  - Equations or correlations are used for VLE computations.
- ✓ Ideal mixture is assumed for simplification of VLE calculations.
  - Generally valid for hydrocarbons that belong to same homologous series.

As we see that the natural gas most of the times have some multi component mixtures that is we have more than two components in the natural gas. So, in such cases, the vapor liquid equilibrium data that is the VLE data are not generally available because of the so many variations in the compositions as well as in the operating conditions. So, we need to have some kind of equations or correlations for estimating the VLE data and the other computations in necessary for such kind of systems.

Now, generally what we do that we assume ideal mixture and as we know that ideal mixture is what that when the both the liquid phase and the vapor phase are ideal. So, when many a times we make this ideal system assumption. So, that we can simplify our computations and analysis and generally, we find that this kind of assumption is valid for the hydrocarbons because in the hydrocarbons, they are generally belong to some homologous series they have similar behavior.

So, we find that this assumption of the ideal system is not too bad.

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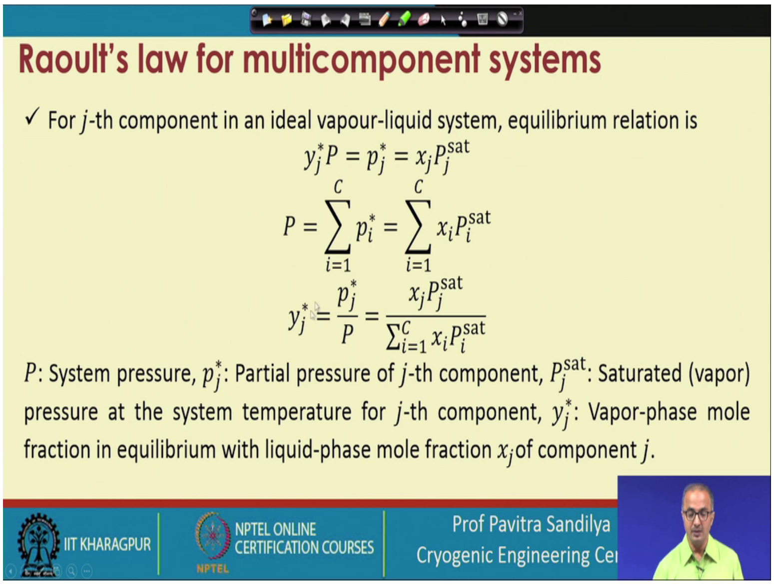

Raoult's law for multicomponent systems

✓ For j-th component in an ideal vapour-liquid system, equilibrium relation is

$$y_j^* P = p_j^* = x_j P_j^{\text{sat}}$$

$$P = \sum_{i=1}^{C} p_i^* = \sum_{i=1}^{C} x_i P_i^{\text{sat}}$$

$$y_j^* = \frac{p_j^*}{P} = \frac{x_j P_j^{\text{sat}}}{\sum_{i=1}^{C} x_i P_i^{\text{sat}}}$$

P: System pressure, p_j^*: Partial pressure of j-th component, P_j^{sat}: Saturated (vapor) pressure at the system temperature for j-th component, y_j^*: Vapor-phase mole fraction in equilibrium with liquid-phase mole fraction x_j of component j.

Now, first we shall go for the Raoult's law for the multi component systems, before we go for that; let us see what the kind of notations you are using here, we are taking P as the system pressure this small pj with a star superscript we are taken as the partial pressure of j th component this star signifies the equilibrium the pj sat is the saturated vapor pressure at the system temperature for the j th component yj star is the vapor phase mole fraction in equilibrium with the liquid phase mole fraction xj of the component j.

So, considering one single component some arbitrary component j, we shall be writing the Raoult's law for the multi component mixture here we must understand this pj star and the yj star are 1 and the same there are two different ways of representing the vapor phase composition. So, let us start with the equilibrium relationship for the j th component, considering ideal vapor and liquid system so; that means, in this case, as we learnt earlier that we have activity coefficients the fugacity coefficient for the non ideal mixtures, if we keep the values of these two coefficients as unity, we shall be getting this particular equation.

Here we find that y star j into p is nothing, but the partial pressure of the component j in the vapor phase is equal to the product of the mole fraction in the vapor liquid phase of the j th component and the saturated vapor pressure and this particular thing is a function of the temperature of the system. Now if we rearrange this equation what we find that the summation of the partial pressures is equal to the total pressure this is coming from the Dalton's law.

So, Dalton law says that the summation of partial pressure is equals to the total pressure and; that means, we are also summing up this particular term on the right hand side and this summation is done for component one to component C the; that means, there are C number of components in the mixture. So, once you know this, now we rearrange this equation this yj is equal to pj by p and in this case, the p is replaced by this particular factor and pj by this particular thing.

So, we find that this yj is now represented in terms of the mole fraction of j th component in the liquid phase the and the saturated vapor pressure of the j th component at the system temperature.

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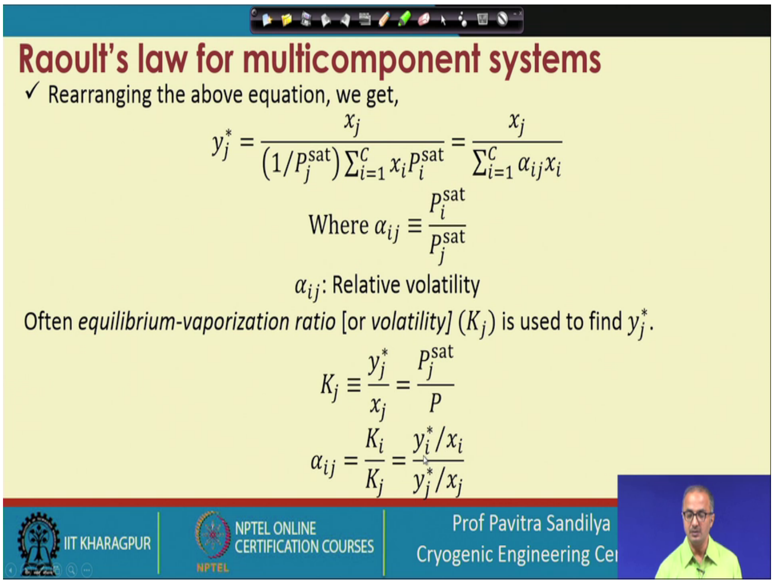

Raoult's law for multicomponent systems

- ✓ Rearranging the above equation, we get,

$$y_j^* = \frac{x_j}{(1/P_j^{\mathrm{sat}})\sum_{i=1}^{C} x_i P_i^{\mathrm{sat}}} = \frac{x_j}{\sum_{i=1}^{C} \alpha_{ij} x_i}$$

Where $\alpha_{ij} \equiv \frac{P_i^{\mathrm{sat}}}{P_j^{\mathrm{sat}}}$

α_{ij}: Relative volatility

Often *equilibrium-vaporization ratio* [or *volatility*] (K_j) is used to find y_j^*.

$$K_j \equiv \frac{y_j^*}{x_j} = \frac{P_j^{\mathrm{sat}}}{P}$$

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{y_i^*/x_i}{y_j^*/x_j}$$

Now, what we do just we rearrange the equation and we slightly do this thing that we divide by this Pj sat and we write for all component and then we when we do this what we find we have this particular new variable this is the relative volatility which is defined as the Pi sat by Pj sat. So, this is true for the ideal system.

So, in now we are representing this yj in terms of the relative volatility now here we have this what we call this equilibrium vaporization ratio or volatility kj which is defined at yj star by xj equal to Pj sat by P or this can be also be written as. So, that is volatility as Ki by kj and this is how we are getting this in terms of the mole fractions of the component i and component j in the vapor and a liquid phase respectively.

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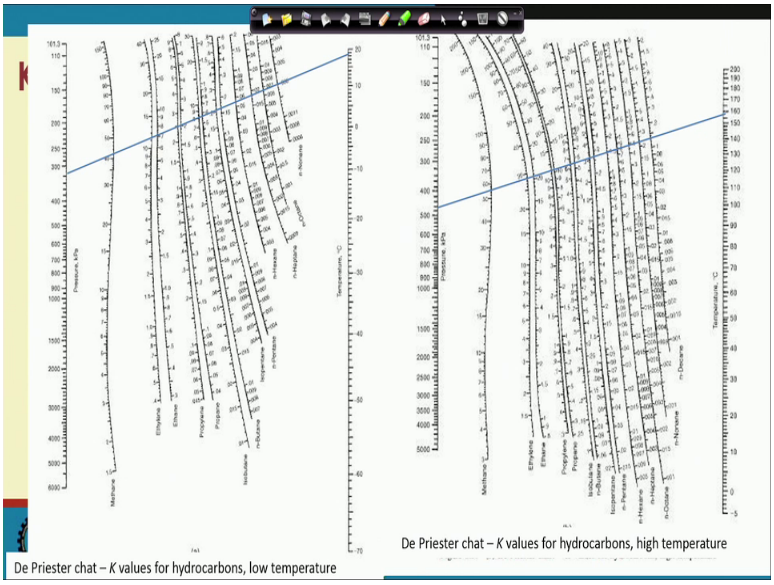

De Priester chat – *K* values for hydrocarbons, low temperature

De Priester chat – *K* values for hydrocarbons, high temperature

Now, this K values may be obtained from various sources and especially for the hydrocarbons there is this De Priester chart, this De Priester chart gives the K value directly for such kind of hydrocarbons especially lower hydrocarbons. So, these are given in many standard books on the thermodynamics or petroleum. So, here are the De Priester charts this particular chart is applicable to find out the k values of hydrocarbons for low temperature.

And here we what we find that on the right hand side this is the temperature axis, which is given in degree centigrade and on the left hand side we have the pressure which is given in Kilo Pascal and here these various curves which you see here, this pertain to the K values of different components like here we have the methane and ethylene ethane propylene propane and so on and so forth.

Now, if we want to find out the K value for any one of these components what we have to do for a we have to first locate the temperature on this axis and the pressure on this axis and let us see what we do suppose, we take this particular temperature and this particular pressure, we simply join these 2 points and we choose for whichever component, we want to know the K value, suppose, I want to know from methane, I just simply read out the value from here that will be the K value of methane for this temperature and this particular pressure.

So, this is quite straightforward and very easy to use only thing is this this particular things cannot be taken directly for any kind of modeling or simulation or computer coding. So, then in that case we have to develop some kind of correlations from this data now this De Priester chart is also available for high temperature. In this case, we see that the lowest temperature is minus 5 degree centigrade and highest is the 200 degree centigrade on this one; we found the lowest temperature was minus 70 degree centigrade and this was 20 degree centigrade.

So, dependent; so, using these two De Priester charts we find that we can span a very large range of temperatures on the other hand, the pressure ranges are remaining almost the same it is starting from 101.3 KPa on both the sides that is about one atmosphere, this one is going up to 6000 KPa and whereas, this is going up to 5000 KPa. Now to again we find that we have the various curve for the various hydrocarbons like methane ethylene ethane propylene, etcetera and the similar manner as we have just learned that we locate the some temperature on this axis and some pressure on this axis.

And when we join these two points we get this kind of a line and then we choose which for whichever hydrocarbon we want to find out the K value we simply read out the point of intersection here suppose we are going for this ethane. So, I simply read out the value at this point. So, this will give me the K value of the particular component and in this case it is ethane. So, this we find that this is very straightforward way of using the De Priester chart.

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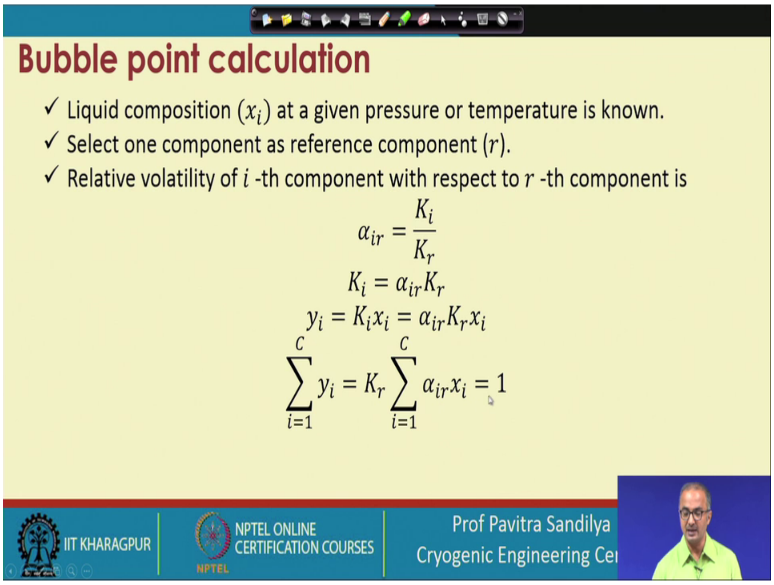

Bubble point calculation

- ✓ Liquid composition (x_i) at a given pressure or temperature is known.
- ✓ Select one component as reference component (r).
- ✓ Relative volatility of i -th component with respect to r -th component is

$$\alpha_{ir} = \frac{K_i}{K_r}$$

$$K_i = \alpha_{ir} K_r$$

$$y_i = K_i x_i = \alpha_{ir} K_r x_i$$

$$\sum_{i=1}^{C} y_i = K_r \sum_{i=1}^{C} \alpha_{ir} x_i = 1$$

Now, with this knowledge of how to find out the k and the alpha that is relative volatility we are now ready to again go back to the bubble point calculation dew point calculation which we did earlier for the binary systems. Now in this case, what let us what we find that suppose we say for the bubble point means that we are given the liquid phase composition we have to find out the vapor phase composition when the first bubble of the liquid gets formed at a given temperature and pressure.

So; that means, in this case we are given the liquid phase composition at any given pressure or temperature. So, if it is given at a pressure and then we have to find the temperature if we are given the temperature then we have to find out the pressure the details of these things we have done earlier for the binary systems and they can be extended for the multi component systems and only thing is that there will be a slight modification in this analysis.

In this case, unlike the binary systems what we are doing here we are choosing a reference component and which is represented by this small r and then what we are doing we are finding the relative volatility of all the components in the mixture with respect to the reference components like this that is we are writing alpha ir equal to Ki by Kr; obviously, in this case if the r is also part of the mixture. So, alpha rr will be equal to unity.

Now, here we find that Ki is equal to alpha ir into Kr. So, yi equal to Ki xi that is the equilibrium relationship and then we replace this Ki in terms of Kr and alpha ir. So, we take the summation as we did earlier for the bubble point calculation, the outer series summation, we obtain this particular equation that is Kr summation of alpha ir xi is equal to 1.

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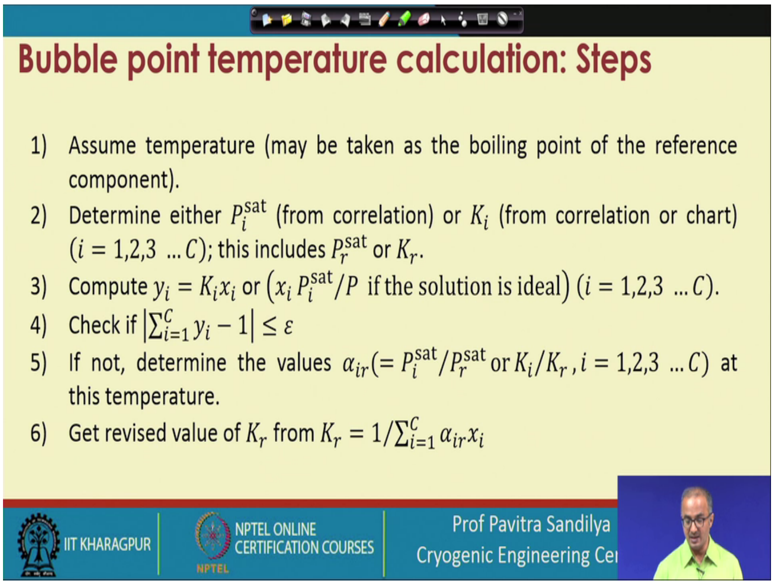

Bubble point temperature calculation: Steps

1) Assume temperature (may be taken as the boiling point of the reference component).
2) Determine either P_i^{sat} (from correlation) or K_i (from correlation or chart) ($i = 1,2,3 \dots C$); this includes P_r^{sat} or K_r.
3) Compute $y_i = K_i x_i$ or $\left(x_i P_i^{sat}/P \text{ if the solution is ideal}\right)$ ($i = 1,2,3 \dots C$).
4) Check if $\left|\sum_{i=1}^{C} y_i - 1\right| \le \varepsilon$
5) If not, determine the values $\alpha_{ir}(= P_i^{sat}/P_r^{sat}$ or $K_i/K_r, i = 1,2,3 \dots C)$ at this temperature.
6) Get revised value of K_r from $K_r = 1/\sum_{i=1}^{C} \alpha_{ir} x_i$

Now, to do this calculation of bubble point these are the following steps here, we are taking the example of bubble point temperature calculation that is we are given the pressure and the liquid phase mole fractions of all the components.

So, let us assume some temperature and this first assumption may be taken as the boiling point of the reference component. Now once we know that as you know temperature, what we can do now? Now we can find out the value of the saturated vapor pressure from some correlation for example, antonin correlation. So, we use some kind of correlation to find out the vapor pressure or we can find directly the value of the Ki if we have say De Priester kind of chart or we have some other kind of correlation.

And this I will go from 1 to C and this includes the reference component as well after finding the pi sat or Ki then what we do we find the value of the yi with the value of this Ki and xi or from this relationship assuming the ideal gas and liquid. So, Pi sat by P and this is also goes for all the components from one to C, then what we do we check that whether the summation of all the y; that means, the mole fractions in the vapor phase is equal to one or not in this case we take the absolute value of this difference and this we take as the summation that is epsilon; epsilon is an user defined convergence criterion to figure out that whether we have reached the solution or not.

Now, if we find that this is not true then what we will do we have to again go back to do the iterations. So, in this case what we do again we find out the new value of the alpha ir and that is done by Pi sat by pr sat or Ki by Kr at the particular temperature we assumed now here we are revising the value of the K Kr by taking this one by this particular thing and this we have already derived that is this is nothing, but the summation of the yi.

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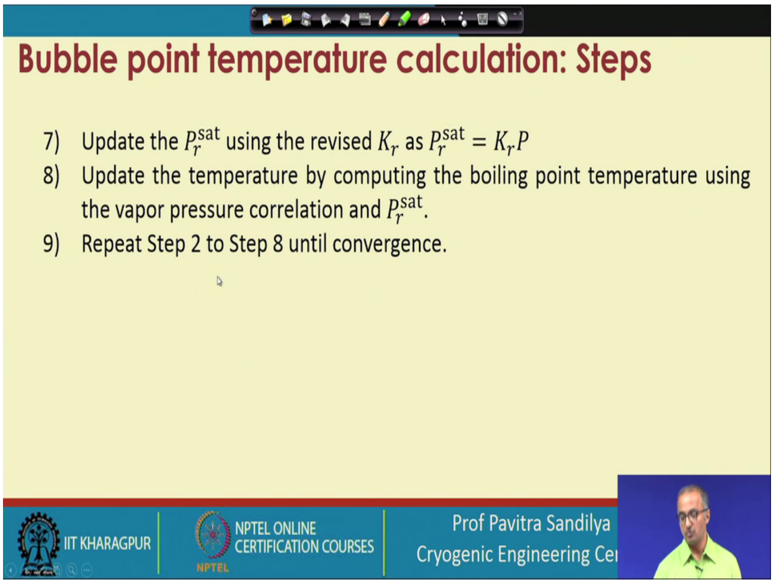

Bubble point temperature calculation: Steps

7) Update the P_r^{sat} using the revised K_r as $P_r^{sat} = K_r P$
8) Update the temperature by computing the boiling point temperature using the vapor pressure correlation and P_r^{sat}.
9) Repeat Step 2 to Step 8 until convergence.

Now, we again update the value of the pr sat that is the saturated vapor pressure of the reference component by this particular equation pr sat equal to Kr into P and then what we do that update the temperature. Now with once, I go to the Pr sat again, I take the correlation for the vapor pressure put this value of that Pr sat there and back, calculate the value of the temperature and this temperature is the updated temperature and we repeat steps 2 to 8 until we go to the convergence.

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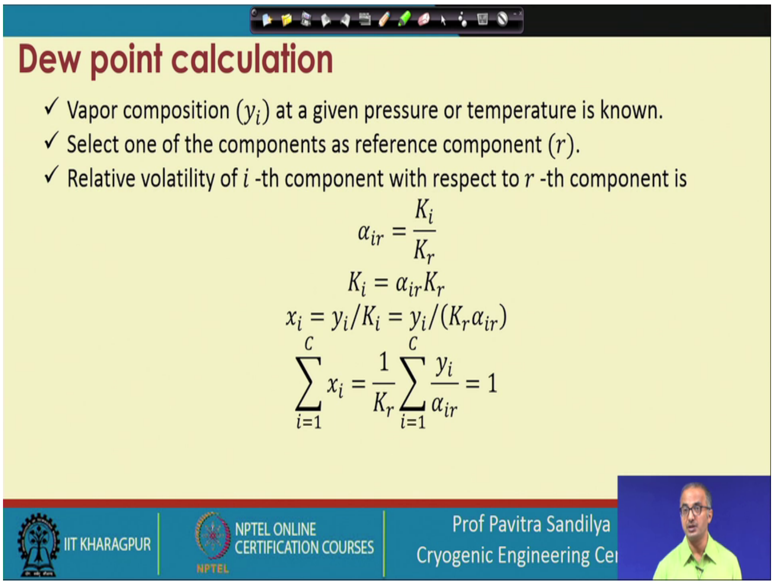

Dew point calculation

- ✓ Vapor composition (y_i) at a given pressure or temperature is known.
- ✓ Select one of the components as reference component (r).
- ✓ Relative volatility of i -th component with respect to r -th component is

$$\alpha_{ir} = \frac{K_i}{K_r}$$

$$K_i = \alpha_{ir} K_r$$

$$x_i = y_i / K_i = y_i / (K_r \alpha_{ir})$$

$$\sum_{i=1}^{C} x_i = \frac{1}{K_r} \sum_{i=1}^{C} \frac{y_i}{\alpha_{ir}} = 1$$

Now, we come to the dew point calculation, in this case we know that this is the temperature at a given pressure when the vapor will form the first liquid drop so; that means, we are given the vapor composition yi at a given pressure or temperature as we did earlier here also we select one of the components as the reference component and we define the relative volatility of all the component with respect to the reference component.

Here it is a slight modification in the equations that Ki equal to alpha ir Kr. Now, we are writing xi which is unknown to us in terms of yi and the Ki and then we again take the summation of this xi which is equal to one and here we have substituted for Ki alpha ir Kr. So, we get this particular equation for the summation of the i and if we are reaching a solution then it must be equal to 1.

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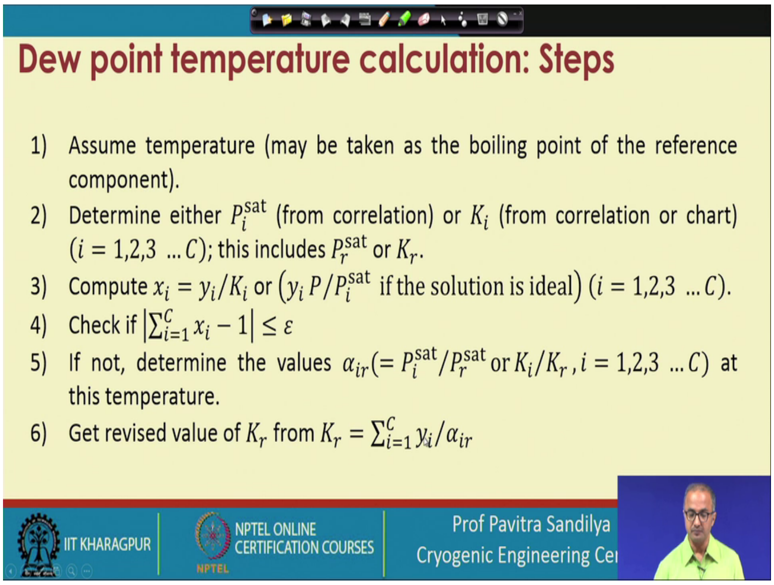

Dew point temperature calculation: Steps

1) Assume temperature (may be taken as the boiling point of the reference component).
2) Determine either P_i^{sat} (from correlation) or K_i (from correlation or chart) $(i = 1,2,3\ \ldots C)$; this includes P_r^{sat} or K_r.
3) Compute $x_i = y_i / K_i$ or $\left(y_i\, P / P_i^{sat}\right.$ if the solution is ideal$\left.\right)$ $(i = 1,2,3\ \ldots C)$.
4) Check if $\left|\sum_{i=1}^{C} x_i - 1\right| \leq \varepsilon$
5) If not, determine the values $\alpha_{ir}(= P_i^{sat}/P_r^{sat}$ or $K_i/K_r\, , i = 1,2,3\ \ldots C)$ at this temperature.
6) Get revised value of K_r from $K_r = \sum_{i=1}^{C} y_i / \alpha_{ir}$

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Now, we see the steps which are used to calculate the dew point temperature and here we first assume the temperature again we this can be taken as the boiling point of the reference component and we find the value of the Pi sat from some correlation or Ki from some chartered correlation for all the components at this assumed temperature and this includes the values of the reference component as well.

Now, we compute the value of the xi from this relationship and for all the components and then we add them up and find out whether it is matching with one or not and if not. So, what we do we determine this alpha ir from this particular equations and once we find this thing then we revise the value of Kr from this particular equation.

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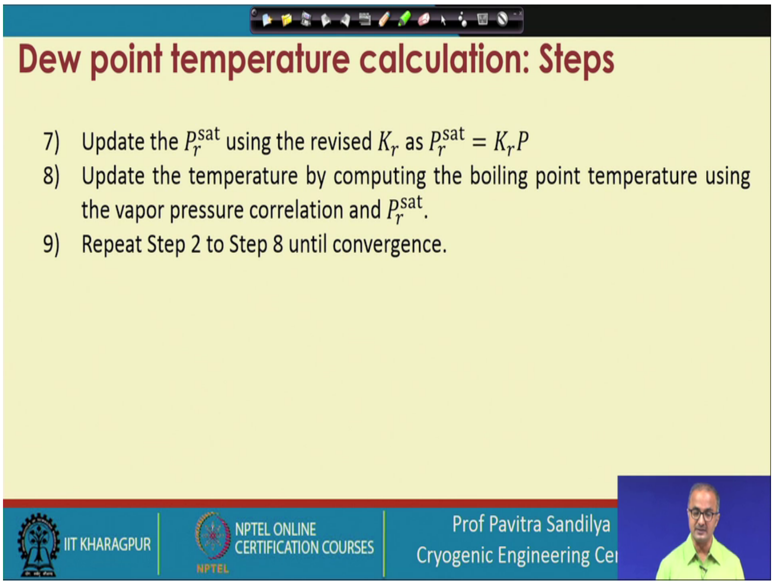

Dew point temperature calculation: Steps

7) Update the P_r^{sat} using the revised K_r as $P_r^{sat} = K_r P$
8) Update the temperature by computing the boiling point temperature using the vapor pressure correlation and P_r^{sat}.
9) Repeat Step 2 to Step 8 until convergence.

And after finding the Kr value as earlier we again update the value of the pr sat in terms of pressure and this updated value of the Kr and once we gotten the value of the Pr sat, we can back calculate the boiling point temperature of the reference component from the given correlation of the vapor pressure, and we repeat steps 2 to 8 until we reach the convergence.

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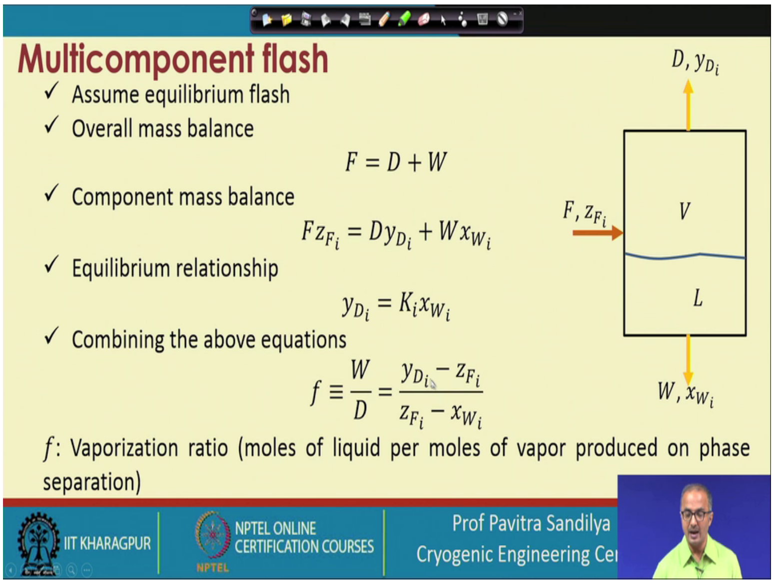

Multicomponent flash

- ✓ Assume equilibrium flash
- ✓ Overall mass balance

$$F = D + W$$

- ✓ Component mass balance

$$F z_{F_i} = D y_{D_i} + W x_{W_i}$$

- ✓ Equilibrium relationship

$$y_{D_i} = K_i x_{W_i}$$

- ✓ Combining the above equations

$$f \equiv \frac{W}{D} = \frac{y_{D_i} - z_{F_i}}{z_{F_i} - x_{W_i}}$$

f: Vaporization ratio (moles of liquid per moles of vapor produced on phase separation)

Next, we go to the multi component flash this, we also learnt for binary systems here with a flash your that the feed is coming and then this feed is after is flashed it is; that means, it is partially vaporized and it goes into two phases and if it is a liquid phase, it will be partially vaporized, it is a vapor feed, then it will be partially liquefied. So, we get two phases out of this thing feed and the liquid phase has a say w is the flow rate of the liquid phase, we take x W i is the mole fraction of the i th component in the liquid phase and d is the vapor phase and y D i is the mole fraction of i th component in the vapor phase.

With this what we do now we write the equilibrium flash we assume ok; that means, we are assuming that this D and W are coming to equilibrium and then we write the overall material balance like f equal to d plus w at steady state and we write the component mass balance also at steady state in terms of this particular mole fractions. Now we use the equilibrium relationship that is y D i equal to K i into x W i and we combine these equations these 2 equations to get something called the vaporization factor f, which is W by D and this is equal to given by given in terms of the mole fractions of the vapor the liquid and the feed.

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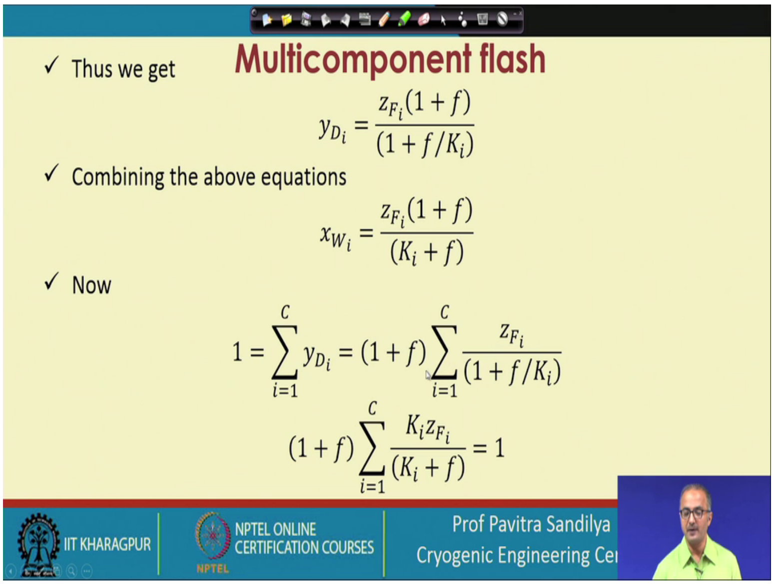

Multicomponent flash

- ✓ Thus we get

$$y_{D_i} = \frac{z_{F_i}(1+f)}{(1+f/K_i)}$$

- ✓ Combining the above equations

$$x_{W_i} = \frac{z_{F_i}(1+f)}{(K_i+f)}$$

- ✓ Now

$$1 = \sum_{i=1}^{C} y_{D_i} = (1+f)\sum_{i=1}^{C} \frac{z_{F_i}}{(1+f/K_i)}$$

$$(1+f)\sum_{i=1}^{C} \frac{K_i z_{F_i}}{(K_i+f)} = 1$$

And thus we get y D i in terms of the f value and Ki and z F i in this. Now we also can get the value of x W i because x W i is y D i by Ki. So, we are modifying this particular equation and ultimately when we take the summation of all the y D is this should be equal to 1 and now, we find on the right hand side we have f and we have Ki and we have Z F i this is given to us and we have to find out the value of the f and Ki.

So, these things we have to solve for to know that how much is the f; that means, what is the ratio of the liquid and the vapor generated after the flash and the value of the Ki.

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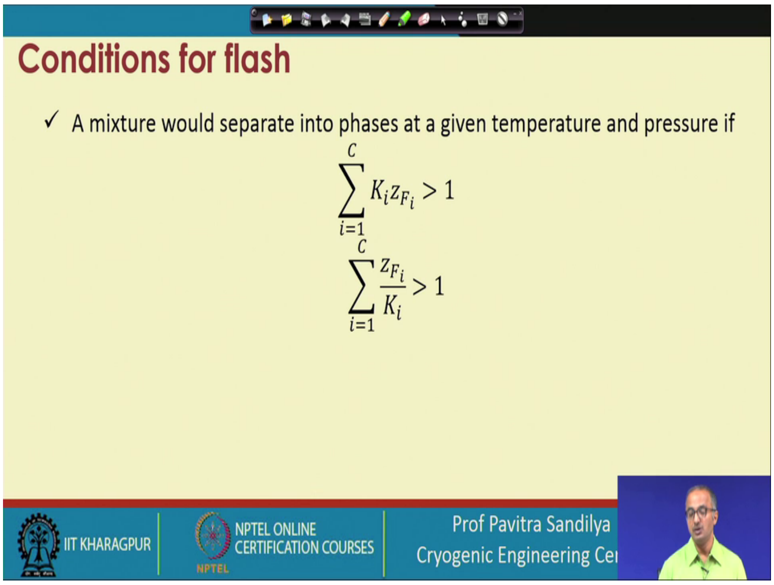

Conditions for flash

✓ A mixture would separate into phases at a given temperature and pressure if

$$\sum_{i=1}^{C} K_i z_{F_i} > 1$$

$$\sum_{i=1}^{C} \frac{z_{F_i}}{K_i} > 1$$

Now, before we go to the flash calculations, you have to ensure that we are having a two phase mixture. So, what we do we do this kind of checking that Ki Z F i is more than this summation we take should be more than 1. Similarly, Z F i by Ki from going from i to C, it should also be more than one if these 2 conditions are satisfied, then only we go for the flash calculation because otherwise we will not be getting two phases.

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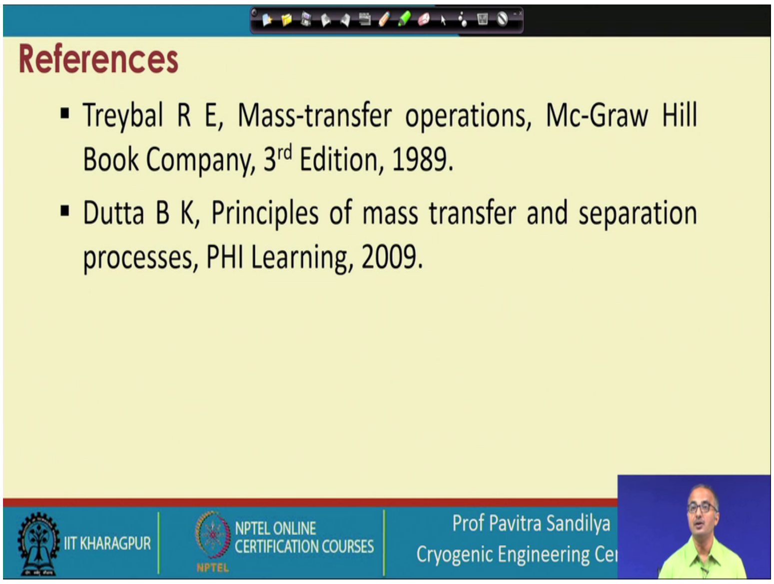

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- Treybal R E, Mass-transfer operations, Mc-Graw Hill Book Company, 3rd Edition, 1989.
- Dutta B K, Principles of mass transfer and separation processes, PHI Learning, 2009.

So, for knowing these fundamentals you can refer to these two books.

Thank you.