Upstream LNG Technology
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Lecture – 07
Dew Point and Bubble Point Calculations

Welcome back. Today, we are going to learn; how to estimate the dew point and bubble point temperatures and pressures. This dew point and bubble point, we covered in the last lecture. So, today we shall see how to estimate these values.

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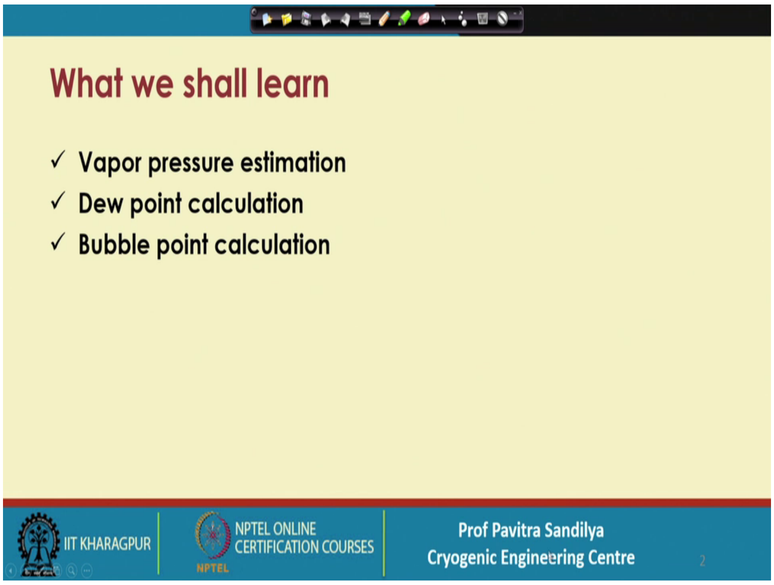

What we shall learn

- ✓ Vapor pressure estimation
- ✓ Dew point calculation
- ✓ Bubble point calculation

So, in this lecture, we shall be learning first the vapor pressure calculation because vapor pressure is one which is needed in the calculation of the dew point and bubble point temperature or pressure, then we shall go to dew point calculation and then bubble point calculation.

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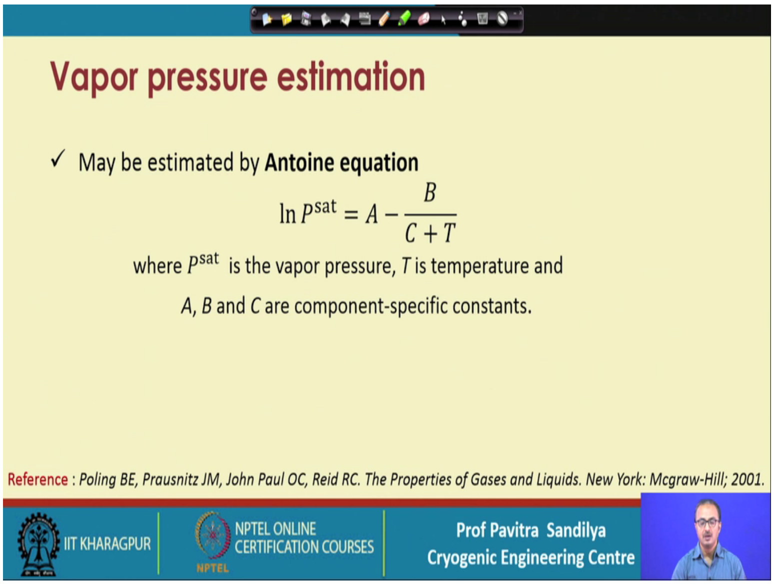

Vapor pressure estimation

- ✓ May be estimated by **Antoine equation**

$$\ln P^{sat} = A - \frac{B}{C + T}$$

where P^{sat} is the vapor pressure, T is temperature and A, B and C are component-specific constants.

Reference : *Poling BE, Prausnitz JM, John Paul OC, Reid RC. The Properties of Gases and Liquids. New York: Mcgraw-Hill; 2001.*

First, the vapor pressure estimation, there are many many correlations which have been developed to estimate the vapor pressure and these correlations are based on experimental data. One of the most popular vapor pressure correlation is Antoine equation. This Antoine equation is also used to estimate the vapor pressure for the components in the natural gas.

The equation has this form on the left hand side; we have the logarithmic of the saturated pressure or the vapor pressure of a liquid. On the right hand side we have 3 parameters; A, B and C which are specific to a given component and here we have T that is the temperature; as we learnt earlier that the vapor pressure is a function of the temperature and is specific to a given component.

Now, at below we are showing the reference which may be referred to get the values of A, B and C. Please note that whenever you are using a correlation, you should be aware of the units being used in the particular correlation. And this Antoine equation and its parameter values have been reported in various literature and sometimes, we have find that it is coming in terms of natural logarithm and sometimes, you can find this logarithm is base 10.

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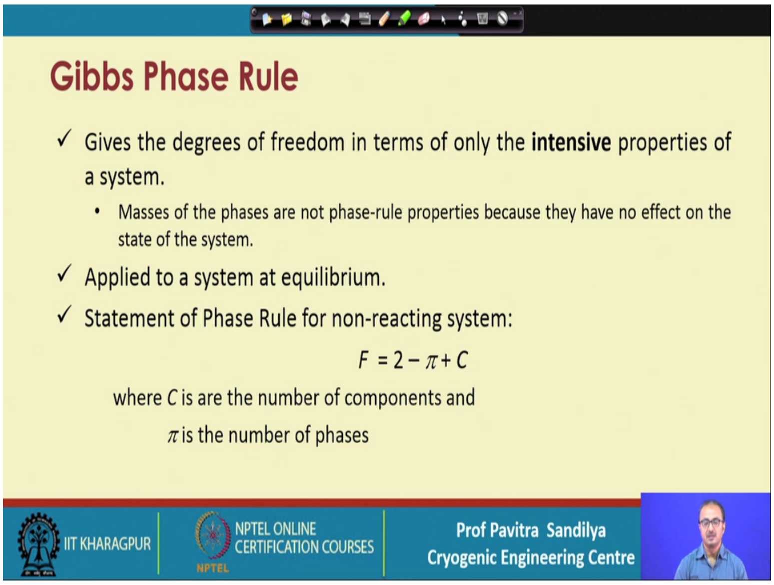

Gibbs Phase Rule

- ✓ Gives the degrees of freedom in terms of only the **intensive** properties of a system.
  - Masses of the phases are not phase-rule properties because they have no effect on the state of the system.
- ✓ Applied to a system at equilibrium.
- ✓ Statement of Phase Rule for non-reacting system:

$$F = 2 - \pi + C$$

where C is are the number of components and

π is the number of phases

Next, we come to Gibbs phase rule. Now, this phase rule is a subset of the degrees of freedom and by degrees of freedom, we mean that the minimum number of properties that must be prescribed to describe a given system and why this is necessary. This is because any system has many many properties with which it may be characterized; however, for practical purposes it is not possible to prescribe the values of all the various properties.

So, it is necessary for us to know what would be the minimum number of properties that must be prescribed to define the particular system. And Gibbs phase rule is a special case which is used to find a degrees of freedom in terms of intensive properties of a system. Here that we mentioned that intensive properties are those properties of a system which do not depend on the mass of the system, for example, density, viscosity, thermal conductivity, etcetera.

In this regard, the masses of the phases are not phase rule properties because it gives only the intensive property. Now Gibbs phase rule is applicable only when the system is at equilibrium, we shall learn about equilibrium in our later lecture. The Gibbs phase rule states that the number of degrees of freedom F is equal to 2 minus pi plus C. In this, the pi is the number of phases and C is the number of components; this particular equation can be derived from basic considerations of the degrees of freedom calculation. The derivation has not been given in this, but it can be found in any standard thermodynamic book.

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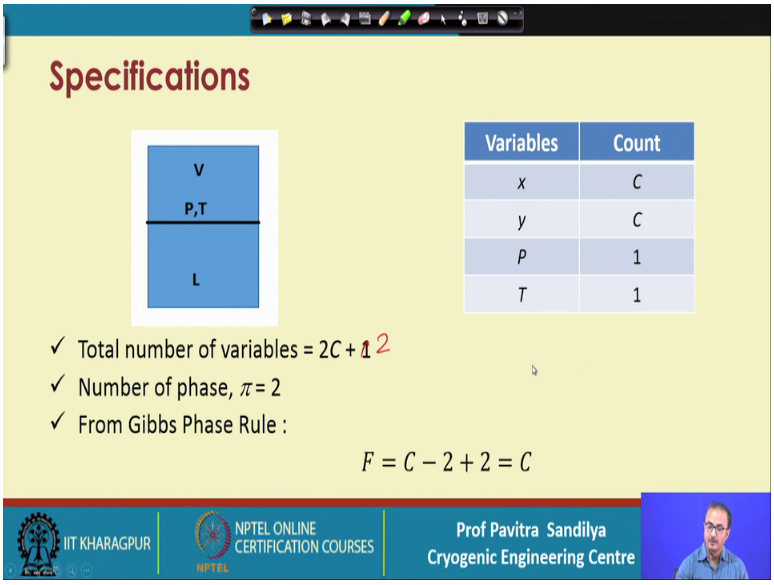

Specifications

Variables	Count
x	C
y	C
P	1
T	1

- ✓ Total number of variables = $2C + \cancel{1}\ 2$
- ✓ Number of phase, $\pi = 2$
- ✓ From Gibbs Phase Rule :

$$F = C - 2 + 2 = C$$

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Now, let us apply the degrees of freedom to a vapor liquid system and this we have shown here; in this figure, in this figure, what it shows that there is a particular system that is a closed system. A closed system is one in which there is mass no mass transfer possible between the system and the surroundings, but the possibility of energy between system and its surroundings is permissible. So, in this closed system, we have a vapor phase and a liquid phase which are in equilibrium and this whole system is characterized by a single pressure and temperature because this is at equilibrium. So, when I say equilibrium it means thermal equilibrium, mechanical equilibrium and chemical equilibrium.

So, when the system is that thermal and mechanical equilibrium, there is a single pressure and a single temperature. So, let us assume that there are C components. Now these C components, now we can say that if we designate by x, the composition or the concentration of each of the components, then we have C number of x variables like x 1, x 2, x 3 like that. Then if y denotes the composition in the vapor phase then for C components, we have C number of concentrations. This concentration maybe in terms of mass fraction, maybe in terms of mole fraction or some similar to those units and then we have one pressure as 1 and 1 temperature as T. So, now, if I count these variables, I will have 2 C plus 2 variables there are 2 C plus 2 variables numb number of phases is 2.

Now, if I apply the Gibbs phase rule, we find that F is equal to C minus 2 plus 2. This 2 comes for the number of phases and so, we find that the degrees of freedom; in this case is C; what it means? It means that to characterize this vapor liquid system with C number of components at equilibrium, we need to specify C number of intensive variables and in this particular table, we have only written the intensive variable.

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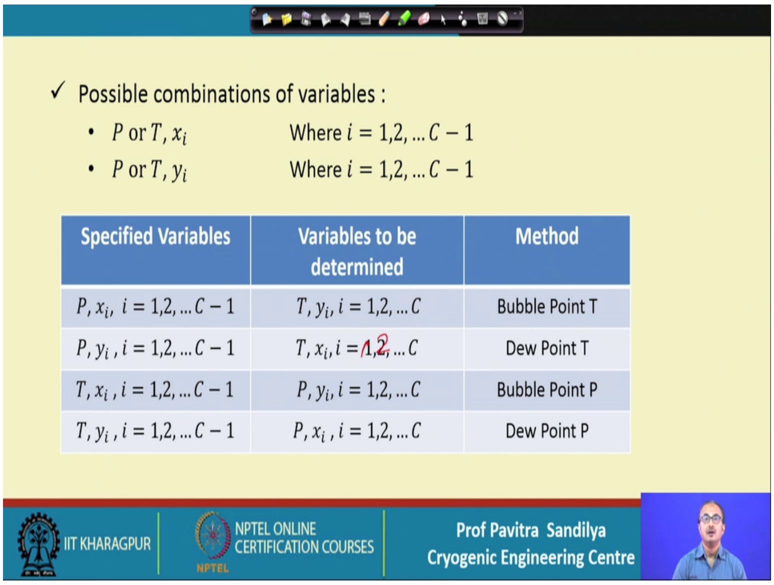

✓ Possible combinations of variables :

- P or T, x_i Where $i = 1,2, \ldots C-1$
- P or T, y_i Where $i = 1,2, \ldots C-1$

Specified Variables	Variables to be determined	Method
$P, x_i,\ i = 1,2, \ldots C-1$	$T, y_i, i = 1,2, \ldots C$	Bubble Point T
$P, y_i, i = 1,2, \ldots C-1$	$T, x_i, i = 1,2, \ldots C$	Dew Point T
$T, x_i, i = 1,2, \ldots C-1$	$P, y_i, i = 1,2, \ldots C$	Bubble Point P
$T, y_i, i = 1,2, \ldots C-1$	$P, x_i, i = 1,2, \ldots C$	Dew Point P

Now, let us see; what are the various possible combinations of these variables which can give me the C degrees of freedom. Now, first here we find; we can prescribe either pressure or temperature and C minus 1 concentrations ok. So, P or temperate temperature T and x i and i goes from 1 to C minus 1. Similarly, I can also prescribe pressure or temperature along with Y i where i goes from 1 to C.

Now, here we see that depending on the type of prescriptions we make we have different types of calculations. So, in this first, we shall see that we have pressure and the C minus 1 concentrations in the liquid phase. So, what we remain to be found out is a temperature and the C number of the vapor phase concentrations.

Now, because we know in this case we know the liquid phase composition and the liquid can only give rise to a vapor. So, we call this as bubble point temperature calculation because we have to find out the temperature. Similarly, we can also prescribe the pressure and the vapor phase concentrations of C minus 1 components in this case, what we find that we have to find out the temperature and the liquid phase composition.

Now, since we are going to find out the temperature and since we have the vapor phase constant concentrations prescribed. So, a vapor can give rise to the liquid. So, the vapor going to liquid, it happens at dew point. So, that that is called dew point temperature calculation, in similar manner, if we are prescribing the temperature and the liquid phase composition for the C minus 1 components.

Then we have to find out the pressure and the vapor phase composition because we are going to find the pressure and because the liquid can again give rise to the vapor, we call it bubble point pressure calculation. And the last combination is that we are prescribing the temperature and the vapor phase composition from which we have to find out the pressure and the liquid phase composition and this, we call it dew point pressure calculation.

So, these are generally the type of calculations, we need to do for a vapor liquid at equilibrium. And as we know once we know the pressure and temperature and the composition, we can find out all other properties; that means, with these prescriptions we are able to characterize a system completely.

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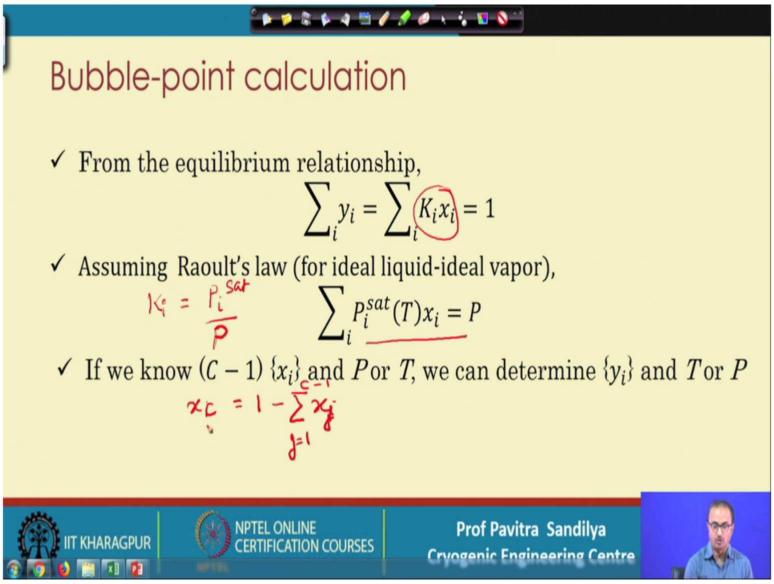

Bubble-point calculation

- ✓ From the equilibrium relationship,

$$\sum_i y_i = \sum_i K_i x_i = 1$$

- ✓ Assuming Raoult's law (for ideal liquid-ideal vapor),

$$K_i = \frac{P_i^{sat}}{P}$$

$$\sum_i P_i^{sat}(T) x_i = P$$

- ✓ If we know $(C-1)$ $\{x_i\}$ and P or T, we can determine $\{y_i\}$ and T or P

$$x_C = 1 - \sum_{j=1}^{C-1} x_j$$

Now, let us go to the bubble point calculation. In the bubble point calculation, I said that we are talking about a how a liquid will form a bubble and at what temperature or pressure, it is from the bubble. So, it means that x is are given and we do not know y i. So, what we are doing we are using the summation of y i summation of y i means summation of the mole fractions in the vapor phase and summation of the mole fractions always is 1. So, we are writing summation y i and here we are using the equilibrium relationship equilibrium relationship is y i is equal to K i x i. So, y i equal to K x i, we are putting here and we are getting it 1.

Now, there are many ways of finding out this x i so, this K i sorry. Now, one of the ways is by Raoult's law about which we shall learn later and if from Raoult's law we find that K i is equal to P i sat by P and if I write Raoult's law says that K i is equal to P i sat by P. So, if I put this expression in this equation, then we can get this particular equation. So, on the left hand side, we have P i sat which is a function of temperature and this is the given mole fractions in the liquid phase and we have on the right hand side, the pressure and this summation is being done for all the C number of components.

So, we see that we know the C minus 1 x i from that we can find out the Cth x i; Cth x i is one minus x i the x C we can say x is equal to 1 minus x i or rather I put xj j equal to 1 to C minus 1. So, that is how we can find the mole fraction of the C th component. Now once we know this all the composition in the liquid phase and P or T, we can determine the y i and T or P; that means, T or P means if I know P i will find T, if I know T i will find P. So, this is the general bubble point calculation principle.

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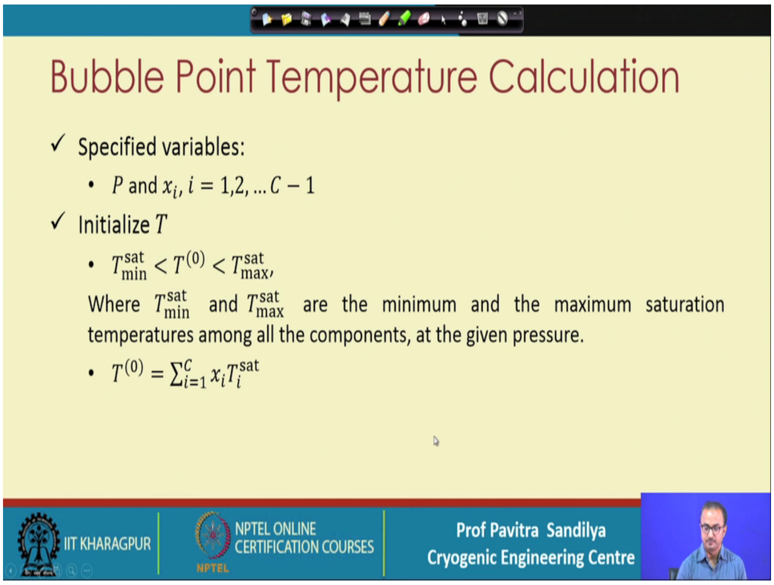

Bubble Point Temperature Calculation

✓ Specified variables:

- P and x_i, $i = 1,2,\dots C-1$

✓ Initialize T

- $T_{\min}^{\text{sat}} < T^{(0)} < T_{\max}^{\text{sat}}$,

Where $T_{\min}^{\text{sat}}$ and $T_{\max}^{\text{sat}}$ are the minimum and the maximum saturation temperatures among all the components, at the given pressure.

- $T^{(0)} = \sum_{i=1}^{C} x_i T_i^{\text{sat}}$

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Now, after knowing this bubble point calculation principle; we go to bubble point temperature calculation, in this, the specified variables are pressure and the liquid phase composition. And from this what we do we have to initialize temperature that is the unknown variable; we have to understand that how to initialize the temperature may be initialized by choosing any arbitrary value. But to if I choose an arbitrary value, it may so happen that in the numerical technique which we are going to use to find out this bubble point temperature may diverge.

So, many of the numerical techniques depend on the initial value we choose to find out the solution. So, to avoid any kind of divergence of the solution; what we do we use some physical understanding it is known that the temperature the dew point temperature and the bubble point temperature will always lie between the maximum and minimum boiling points of the components in a given system. So, we need to know the boiling points of each of the components in the system and this we represent by T sat. So, if for all the components we find the T sat and choose the minimum T sat and the maximum T sat and we choose the initial temperature some value within this particular range.

Now, one way of initializing this temperature is that we take some kind of an average of all the boiling points and this average may be that we take a weighted average the weighted factor being the mole fraction of all the components. So, this may be one starting point to initialize T to do the bubble point temperature calculation.

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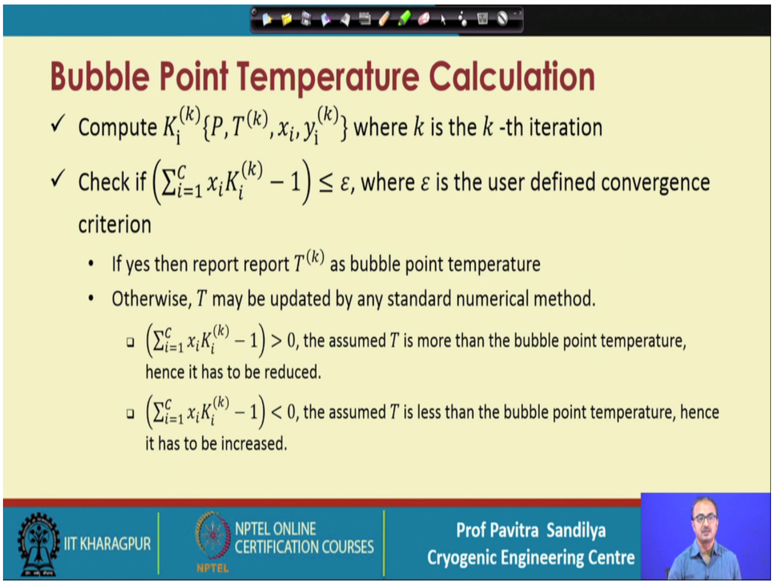

Bubble Point Temperature Calculation

- ✓ Compute $K_i^{(k)}\{P, T^{(k)}, x_i, y_i^{(k)}\}$ where k is the k -th iteration
- ✓ Check if $\left(\sum_{i=1}^{C} x_i K_i^{(k)} - 1\right) \le \varepsilon$, where ε is the user defined convergence criterion
  - If yes then report report $T^{(k)}$ as bubble point temperature
  - Otherwise, T may be updated by any standard numerical method.
    - ❑ $\left(\sum_{i=1}^{C} x_i K_i^{(k)} - 1\right) > 0$, the assumed T is more than the bubble point temperature, hence it has to be reduced.
    - ❑ $\left(\sum_{i=1}^{C} x_i K_i^{(k)} - 1\right) < 0$, the assumed T is less than the bubble point temperature, hence it has to be increased.

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Now, once we have initialized temperature and with the knowledge of pressure and x i and y i k, we can find out the value of the K i; K i is the equilibrium constant about which we shall know in a separate lecture. So, for the time being we understand that we know the K i value in terms of pressure, some assume temperature x i is known and y i is some again intermediate mole fraction of the vapor compose vaporized components and this k as the superscript represents the k th iteration.

Because we are doing a numerical technique, it will be an iterative process. Now, after finding this K and again, we go back to this finding the value of this x i and K i from the previous thing, we find that this equation must be satisfied this particular equation must be satisfied. So, once we find the values of the K i, they we plug in the values of K i and the x i and see that check whether this is going to be equal to 1 or not. So, this will tell if our chosen temperature is the correct temperature, then it will certainly be 1 if it is not one; that means, the chosen temperature is not the right temperature and we have to do the iteration to get the right value.

So, for this what we do that we now go for iteration and these iterations are carried out in the way that this particular value is this absolute value of this particular thing absolute of this should be less than or equal to some user defined convergence criterion. So, depending on the accuracy, we need; we will choose the value of this epsilon and we will try to see that this particular thing comes down or becomes equal to the prescribed convergence criterion, if we find that it is not converging, then we have to update this temperature by some suitable numerical method about which again, we shall be talking later.

Now, how do we know that to choose the next temperature? So, there are some simple criterion criteria first criterion is this that if this particular summation minus 1 comes more than 0; if this comes more than 0, then P is more than the bubble point temperature. So, it has to be reduced on the other hand, if this is less than 0 the assume T is less than the bubble point temperature and hence it has to be increased. So, this way by slightly changing this value of this temperature, we will find that we are able to reach the converged value of T after a few iterations.

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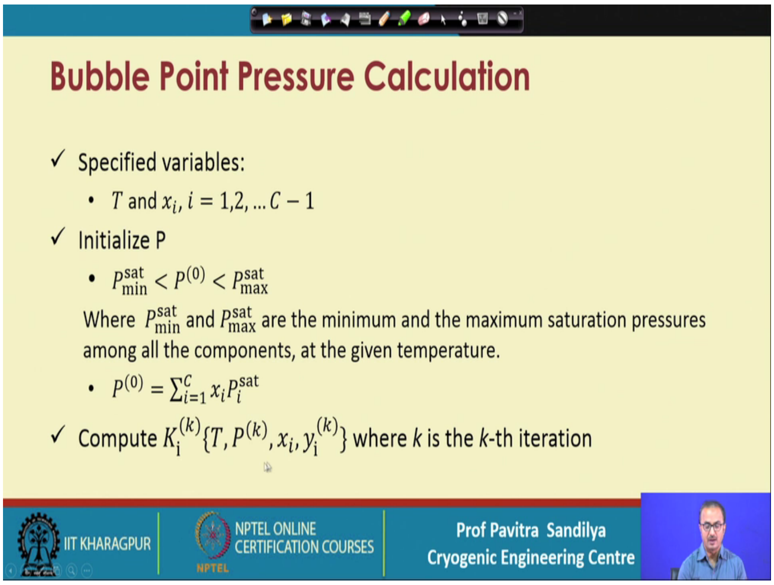

Bubble Point Pressure Calculation

✓ Specified variables:
- T and $x_i, i = 1,2, \dots C - 1$

✓ Initialize P
- $P_{\text{min}}^{\text{sat}} < P^{(0)} < P_{\text{max}}^{\text{sat}}$

Where $P_{\text{min}}^{\text{sat}}$ and $P_{\text{max}}^{\text{sat}}$ are the minimum and the maximum saturation pressures among all the components, at the given temperature.
- $P^{(0)} = \sum_{i=1}^{C} x_i P_i^{\text{sat}}$

✓ Compute $K_{\text{i}}^{(k)}\{T, P^{(k)}, x_i, y_{\text{i}}^{(k)}\}$ where k is the k-th iteration

Similarly, if I go to the bubble point pressure calculation, we will find that in this case the specific variables are T and x i we have to initialize P and in this case, we have to remember that the pressure will lie between the vapor pressure the minimum vapor pressure and the maximum v vapor pressure of all the components.

So, we need to find out the vapor pressure from the given T for all the components and the actual pressure bubble point pressure will be lying between these 2 maximum and minimum vapor pressures; that is why it is important for us to know the vapor pressure of the components. It may be two prescribed here that the Antoine equation may also be used to find out the T sat in the sense that for a given pressure the temperature obtained is the boiling point temperature, similarly, for the given temperature the pressure obtained is the vapor pressure.

So, if I want to know the pressure, I can prescribe give the temperature on the right hand side of Antoine equation and find out the pressure from the left hand side ok. So, that equation is for vapor pressure calculation. And similarly, under the bubble point temperature calculation I prescribed the pressure value and corresponding to that I find the temperature value for the given component that is the P sat of the particular component.

As we did for earlier for the bubble point temperature calculation, again, we have we are having will be having this equation and if our pressure is chosen is correct, then we shall be reaching convergence. Otherwise, we have to repeat the iterations similar to that I am not detailing it, here it is similar to that we are also having the K values and from the K values.

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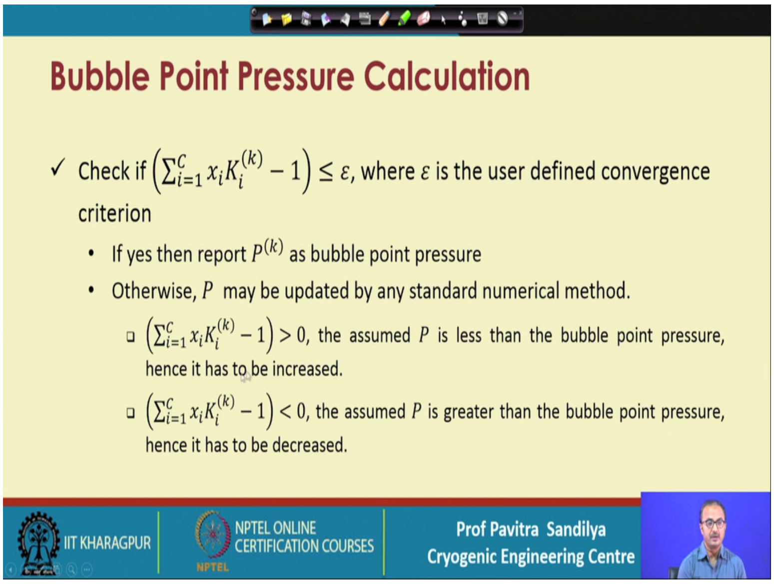

Bubble Point Pressure Calculation

✓ Check if $\left(\sum_{i=1}^{C} x_i K_i^{(k)} - 1\right) \leq \varepsilon$, where ε is the user defined convergence criterion

- If yes then report $P^{(k)}$ as bubble point pressure
- Otherwise, P may be updated by any standard numerical method.
    - ☐ $\left(\sum_{i=1}^{C} x_i K_i^{(k)} - 1\right) > 0$, the assumed P is less than the bubble point pressure, hence it has to be increased.
    - ☐ $\left(\sum_{i=1}^{C} x_i K_i^{(k)} - 1\right) < 0$, the assumed P is greater than the bubble point pressure, hence it has to be decreased.

We shall be finding the, this particular summation. And we shall try to see that this summation here this absolute value is falling within some convergence limit and then we can keep on iterating it till we get the convergence. So, similar to the temperature we can go on adjusting the pressure depending on this particular criterion.

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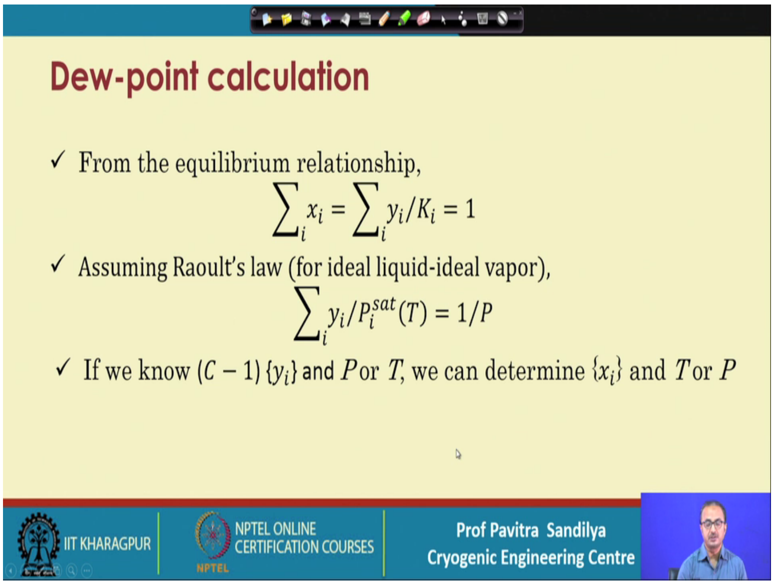

Dew-point calculation

- ✓ From the equilibrium relationship,

$$\sum_i x_i = \sum_i y_i/K_i = 1$$

- ✓ Assuming Raoult's law (for ideal liquid-ideal vapor),

$$\sum_i y_i/P_i^{sat}(T) = 1/P$$

- ✓ If we know $(C-1)$ $\{y_i\}$ and P or T, we can determine $\{x_i\}$ and T or P

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Next, we go to the dew point calculation in this case, we are given the vapor phase composition. So, what we are doing we are adjusting we are rewriting this x which have to be found out we are writing this x in terms of y i and here we are writing this equal to 1. So, with this equilibrium relationship what we are doing now we are substituting for K i P i sat by P and if I readjust this equation I find that we are getting y i by P i sat as a function of temperature is equal to 1 by P. So, this is the governing equation to find out the dew point dew point pressure or dew point temperature.

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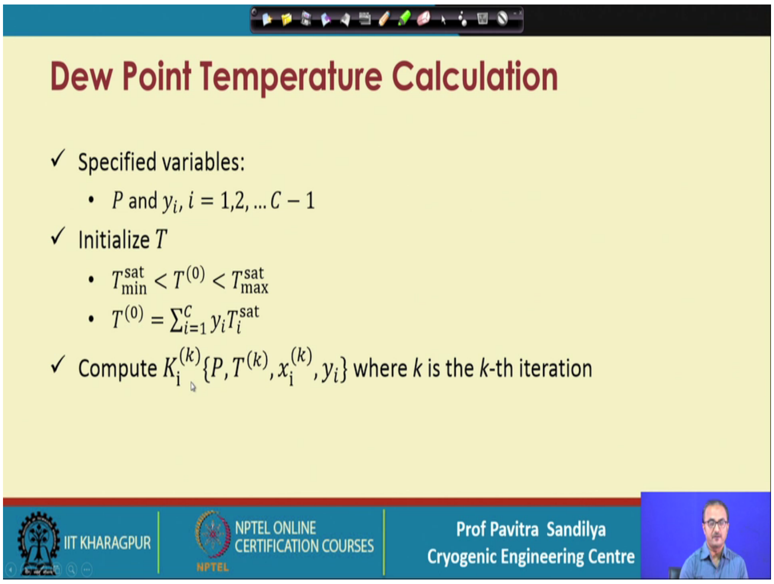

Dew Point Temperature Calculation

- ✓ Specified variables:
  - P and y_i, $i = 1,2, \ldots C-1$
- ✓ Initialize T
  - $T_{\min}^{sat} < T^{(0)} < T_{\max}^{sat}$
  - $T^{(0)} = \sum_{i=1}^{C} y_i T_i^{sat}$
- ✓ Compute $K_i^{(k)}\{P, T^{(k)}, x_i^{(k)}, y_i\}$ where k is the k-th iteration

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Now, first coming to dew point temperature calculation, here the specified variables are pressure and y i with this again you have to initialize T as before and we can initialize T as earlier by choosing some value between the T sat minimum and T sat maximum. And we can apply the same principle to find out the initial value of T and same way we are finding k i and after finding the k i.

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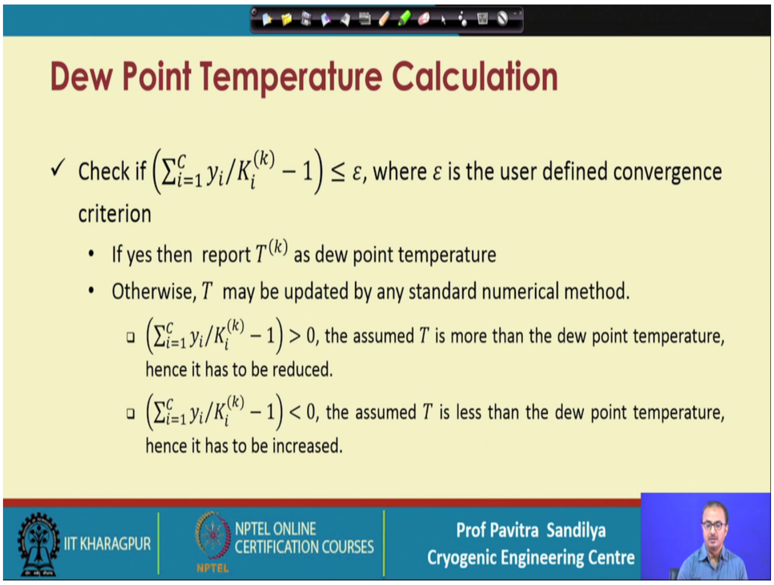

Dew Point Temperature Calculation

✓ Check if $\left(\sum_{i=1}^{C} y_i/K_i^{(k)} - 1\right) \leq \varepsilon$, where ε is the user defined convergence criterion

- If yes then report $T^{(k)}$ as dew point temperature
- Otherwise, T may be updated by any standard numerical method.
  - ☐ $\left(\sum_{i=1}^{C} y_i/K_i^{(k)} - 1\right) > 0$, the assumed T is more than the dew point temperature, hence it has to be reduced.
  - ☐ $\left(\sum_{i=1}^{C} y_i/K_i^{(k)} - 1\right) < 0$, the assumed T is less than the dew point temperature, hence it has to be increased.

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We find this value just note the change on the expression for this. So, we find this value and check that whether this absolute value is within the convergence criterion or not. After doing this what we do that we now go on iterating it till we go with convergence and for updating the value of T, we use the same judgment as before this, I am not describing and we shall do some example problems later to demonstrate how to carry out this dew point and bubble point calculations.

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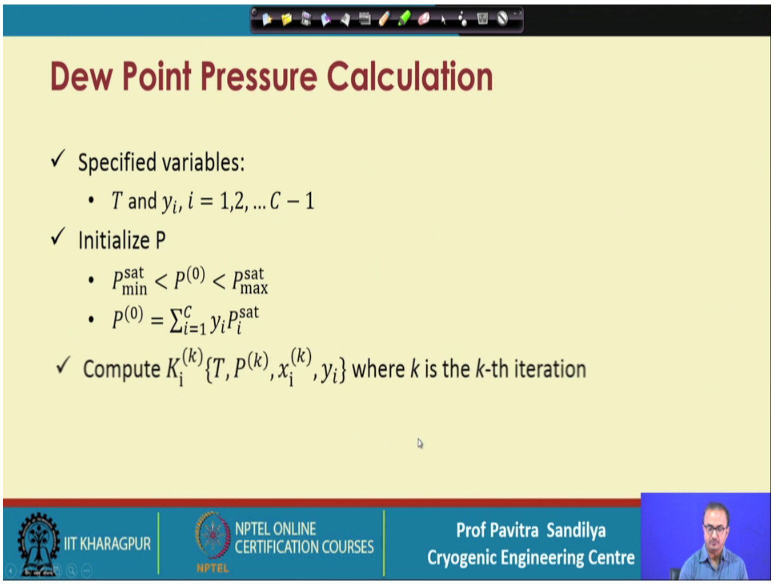

Dew Point Pressure Calculation

- ✓ Specified variables:
  - T and y_i, $i = 1,2, \dots C-1$
- ✓ Initialize P
  - $P^{sat}_{min} < P^{(0)} < P^{sat}_{max}$
  - $P^{(0)} = \sum_{i=1}^{C} y_i P_i^{sat}$
- ✓ Compute $K_i^{(k)}\{T, P^{(k)}, x_i^{(k)}, y_i\}$ where k is the k-th iteration

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Now, here we come to dew point pressure calculation, in this case temperature and the vapor phase compositions are specified and again here we have to initialize the pressure. And we initialize pressure like this as before and we find the overall pressure like this find the value of K i.

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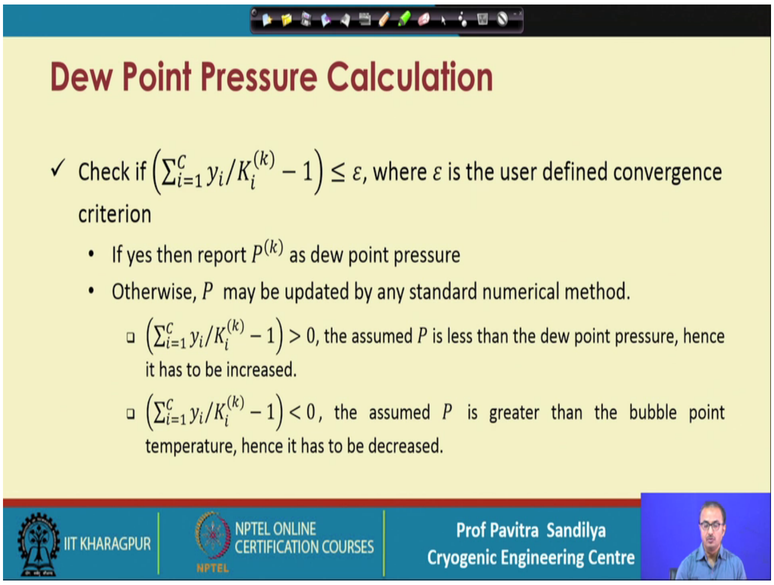

Dew Point Pressure Calculation

- ✓ Check if $\left(\sum_{i=1}^{C} y_i/K_i^{(k)} - 1\right) \leq \varepsilon$, where ε is the user defined convergence criterion
  - If yes then report $P^{(k)}$ as dew point pressure
  - Otherwise, P may be updated by any standard numerical method.
    - ☐ $\left(\sum_{i=1}^{C} y_i/K_i^{(k)} - 1\right) > 0$, the assumed P is less than the dew point pressure, hence it has to be increased.
    - ☐ $\left(\sum_{i=1}^{C} y_i/K_i^{(k)} - 1\right) < 0$, the assumed P is greater than the bubble point temperature, hence it has to be decreased.

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And do the iterations again check for the convergence of the absolute value of this particular expression and if not we are going to again update the value of the pressure and after a few iterations, we will find that we shall be getting the converged value of the pressure.

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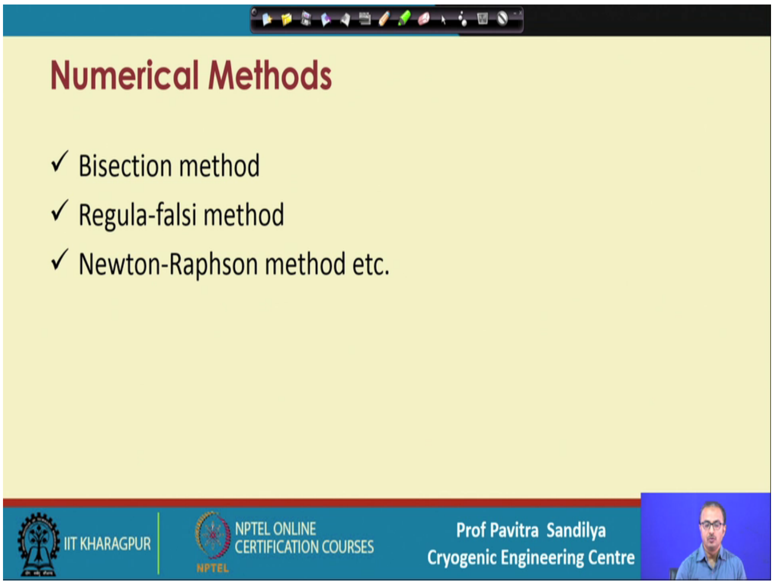

Numerical Methods

- ✓ Bisection method
- ✓ Regula-falsi method
- ✓ Newton-Raphson method etc.

So, this is the way we are going to find out the dew point temperature dew point pressure bubble point temperature bubble point pressure, as I was telling you, we are going to use some numerical techniques and these numerical techniques pertain to solution of equations for finding the roots of equation roots of non-linear algebraic equation. So, I have just listed a few of the methods which are used like bisection method Regula-falsi method and Newton-Raphson method.

There may be many other methods which are given in some standard numerical methods textbook and these materials, you may study further from the 3 books.

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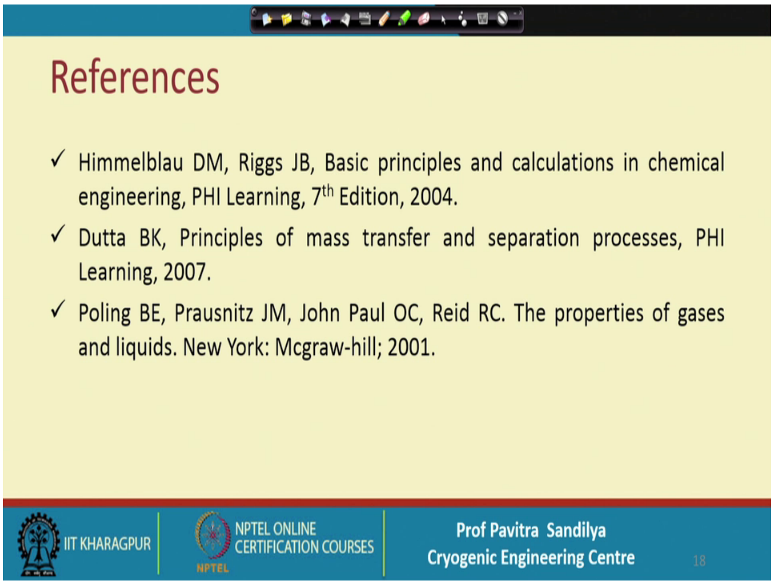

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I have prescribed here these first two books, will give you the principles and the calculations and the third book this by read Prausnitz and this Paul Reid, these are very this is very good resource book to find out the various properties of the gases and liquids. So, with this we come to the end of this lecture.

Thank you.