Upstream LNG Technology
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Lecture - 61
Tutorial on equilibrium in multicomponent systems

Welcome, after learning the fundamentals of the analysis of the multi component systems, today in this lecture; we shall be solving some problems to highlight those methods. So, in this we have the Tutorial on the equilibrium in multi component systems and in this we shall be learning about the bubble point calculation, dew point calculation in multi component systems and multicomponent flash.

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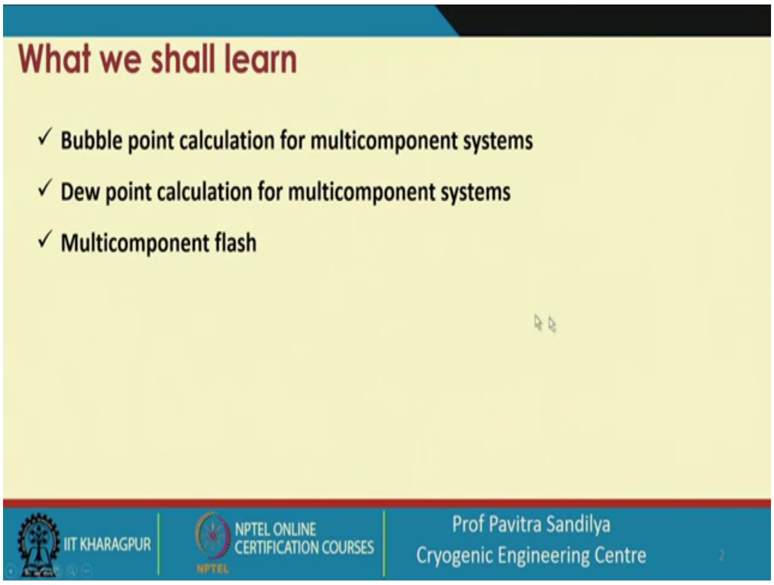

What we shall learn

- ✓ Bubble point calculation for multicomponent systems
- ✓ Dew point calculation for multicomponent systems
- ✓ Multicomponent flash

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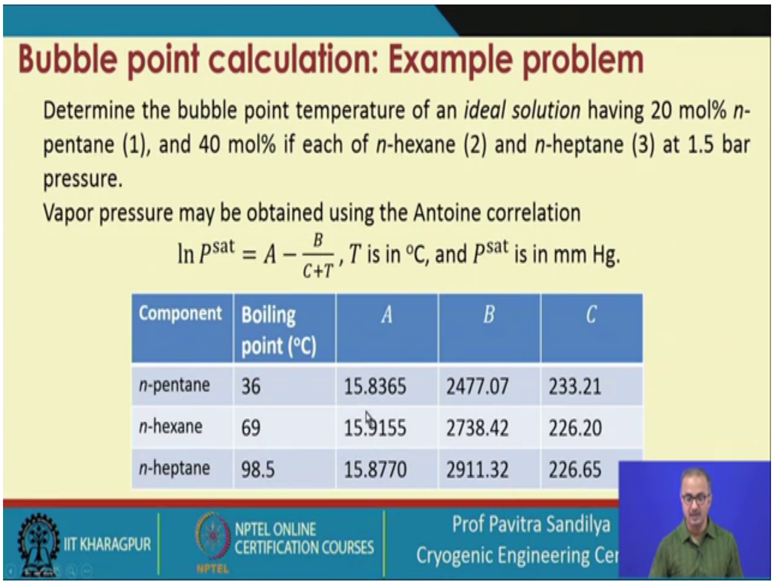

Bubble point calculation: Example problem

Determine the bubble point temperature of an *ideal solution* having 20 mol% *n*-pentane (1), and 40 mol% if each of *n*-hexane (2) and *n*-heptane (3) at 1.5 bar pressure.

Vapor pressure may be obtained using the Antoine correlation

$$\ln P^{sat} = A - \frac{B}{C+T}, T \text{ is in } ^\circ\text{C, and } P^{sat} \text{ is in mm Hg.}$$

Component	Boiling point (°C)	A	B	C
n-pentane	36	15.8365	2477.07	233.21
n-hexane	69	15.9155	2738.42	226.20
n-heptane	98.5	15.8770	2911.32	226.65

So, but first we just take an example of bubble point calculation. In this, we have to determine the bubble point temperature of an ideal solution having 20 mol percent n pentane which is labelled as component 1 and 40 mol percent each of n hexane and n heptane which are labelled as component 2 and component 3 respectively. And the pressure is 1.5 bar.

The vapour pressure we will need to find out the volatility is taken from this particular equation that is the Antoine equation and in these the temperature is in degree centigrade and the pressure is in millimetre of Hg. So, this equation may be used to find out the boiling point at a given pressure or the vapour pressure at a given temperature. And the A B C values will depend on the particular component and these values have been listed in this particular table here. We find for n pentane, hexane, n heptane the boiling points are given and the A B C values are given.

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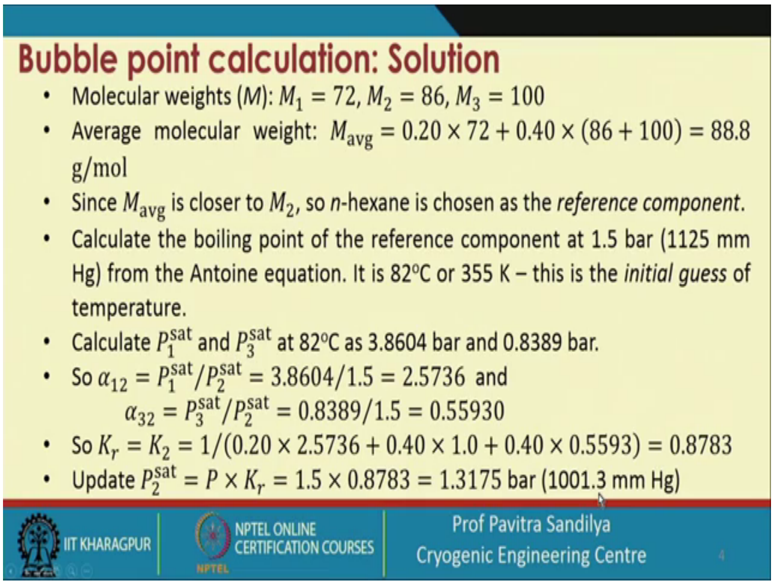

Bubble point calculation: Solution

- Molecular weights (M): $M_1 = 72, M_2 = 86, M_3 = 100$
- Average molecular weight: $M_{avg} = 0.20 \times 72 + 0.40 \times (86 + 100) = 88.8$ g/mol
- Since M_{avg} is closer to M_2, so *n*-hexane is chosen as the *reference component*.
- Calculate the boiling point of the reference component at 1.5 bar (1125 mm Hg) from the Antoine equation. It is 82°C or 355 K – this is the *initial guess* of temperature.
- Calculate P_1^{sat} and P_3^{sat} at 82°C as 3.8604 bar and 0.8389 bar.
- So $\alpha_{12} = P_1^{sat}/P_2^{sat} = 3.8604/1.5 = 2.5736$ and
  $\alpha_{32} = P_3^{sat}/P_2^{sat} = 0.8389/1.5 = 0.55930$
- So $K_r = K_2 = 1/(0.20 \times 2.5736 + 0.40 \times 1.0 + 0.40 \times 0.5593) = 0.8783$
- Update $P_2^{sat} = P \times K_r = 1.5 \times 0.8783 = 1.3175$ bar (1001.3 mm Hg)

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Now, with these information, we shall proceed with the solution first what we do? We list out the molecular weight of each of the components. And then find out the average molecular weight by summing up the product of the mol fraction and the molecular weight of each of the components and we find this is coming out to be 88.8. Here because the n heptane and n hexane has the same composition. So, we are multiplying this 0.4 we are taking out of the bracket and putting their respective molecular weight.

Now, we find that this average molecular weight is closer to M 2 that is n hexane. So, we choose n hexane as the reference component. So, this is the way we choose the reference component in a given mixture by looking at the molecular average molecular weight of the mixture. Now once we have chosen the reference component, what we do? We find the boiling point of the reference component as the first guess for the bubble point temperature.

So, in this case, what we do we at this 1.5 bar pressure as we take this as the vapour pressure and we calculate the temperature from the Antoine equation. And we find that the value comes out to be almost 82 degree centigrade or 355 Kelvin. So, this value is taken as the initial guess temperature. Now what we do we find the vapour pressures of the other two components at this particular temperature again from the Antoine equation and we get these two values respectively for the other two components.

So, here we now find the relative volatility because in the problem, we have been told that we may assume it to be an ideal solution. So, we take with respect to the reference component that is component two, we find out the relative volatilities first with rest for the n pentane and then for the n heptanes. And we find these are the values of the relative volatilities. And looking at these values we find that an n hexane is more volatile than n heptane, but less volatile than n pentane and this is expected because the molecular weight wise n hexane lies between n pentane and n heptanes. And now what we do we find the value of the K r that is the reference value of the K which is equal to K 2 and this is the value of the K r, we find from the particular formula we have given earlier.

And please understand that when we talk a bubble point that means, we are assuming that the given compositions are for the liquid. So, we use this formula x i into this alpha i r that formula we use. So, one by summation of x i into alpha i r that formula we use and we get this as the value of the K r. Once you obtain the value of the K r, now we can again update this values of this P 2 sat that is the vapour pressure of the n hexane. And this we find as 1.3175 bar that is about 1001.3 millimetre of mercury.

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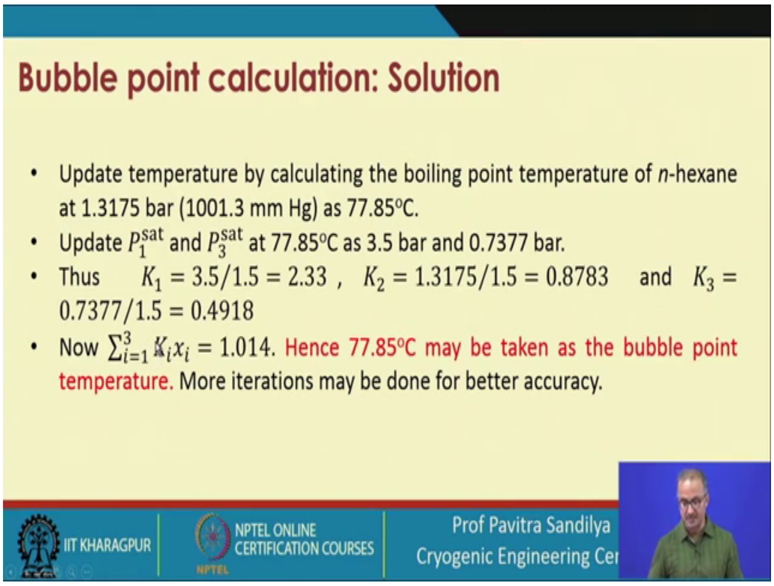

Bubble point calculation: Solution

- Update temperature by calculating the boiling point temperature of *n*-hexane at 1.3175 bar (1001.3 mm Hg) as 77.85°C.
- Update P_1^{sat} and P_3^{sat} at 77.85°C as 3.5 bar and 0.7377 bar.
- Thus $K_1 = 3.5/1.5 = 2.33$, $K_2 = 1.3175/1.5 = 0.8783$ and $K_3 = 0.7377/1.5 = 0.4918$
- Now $\sum_{i=1}^{3} K_i x_i = 1.014$. Hence 77.85°C may be taken as the bubble point temperature. More iterations may be done for better accuracy.

So, this is the updated value of the vapour pressure of n hexane that is the reference component. Once we got that pressure updated pressure again, we go back to the Antoine equation and at that particular pressure we find out the updated temperature as this value 77.85 degree centigrade. And again with this, value what we do? We update the values of the vapour pressures of the other two components and we find the vapour pressures are coming out to be now 3.5 bar and 0.7377 bar.

That means what we are doing basically we are updating the values of the temperature and the pressure by this iteration. So, we have completed one iteration and we updated the values of the temperature and the pressures. Now with these values of the various vapour pressures, we now find out the K 1 K 2 K 3 values like this that we know that P sat by P is the K 1. So, that is the way we K i equal to P i sat by P that is how we are finding the values of the various K is. And once we find the value of K is now what we have need to check.

We need to check that whether this K i x i well it is a summation of this things this must be coming out to be 1 and this is coming out to about 1.014. Now whether we should stop here or whether we should proceed beyond that? It will depend on the accuracy desired by the user. So, somebody can say that we can take this 77.85 as a solution for the bubble point temperature otherwise if we need more accuracy, then we have to repeat this whole procedure again with these values of this (Refer Time: 07:10) with this because again repeat the value procedure like we find the value of alpha K r again a the from that the t is the t value and then K i again we find the value of the K1 K 2 K 3. And again keep checking up this particular summation and that is how we will carry out the iterations.

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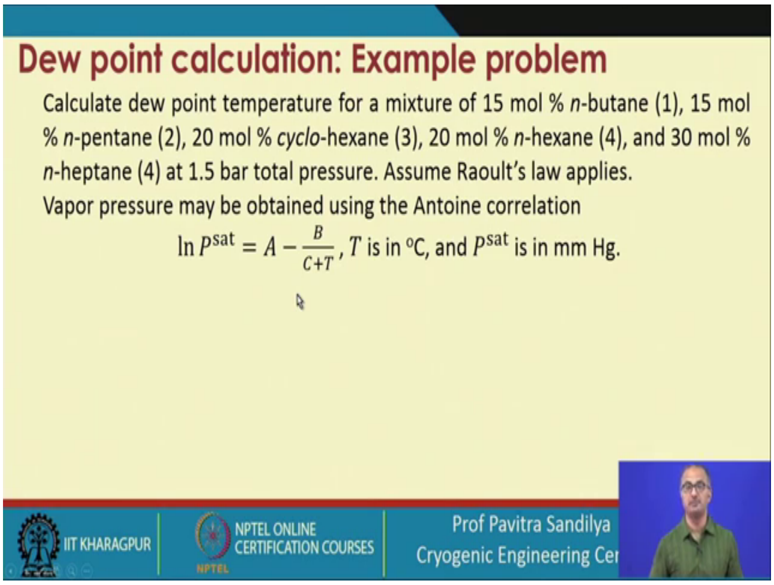

Dew point calculation: Example problem

Calculate dew point temperature for a mixture of 15 mol % *n*-butane (1), 15 mol % *n*-pentane (2), 20 mol % *cyclo*-hexane (3), 20 mol % *n*-hexane (4), and 30 mol % *n*-heptane (4) at 1.5 bar total pressure. Assume Raoult's law applies.

Vapor pressure may be obtained using the Antoine correlation

$$\ln P^{sat} = A - \frac{B}{C+T}, T \text{ is in } ^{o}\text{C, and } P^{sat} \text{ is in mm Hg.}$$

In similar fashion we go to a Dew point calculation problem. In this we have been asked to determine the Dew point temperature in a mixture with the mixture contains 15 mol percent of n butane which is labelled as one component 1. Then 15 mol percent of n pentane component 2, 20 mol percent of cyclo hexane component 3, 20 mol percent of n hexane component 4 and 30 mol percent of n heptane component 5; this will be component 5 at 1.5 bar total pressure.

And we are asked that we can assume the Raoult's law like the or we are question and we have been given this Antoine equation to find out the vapour pressures of the components.

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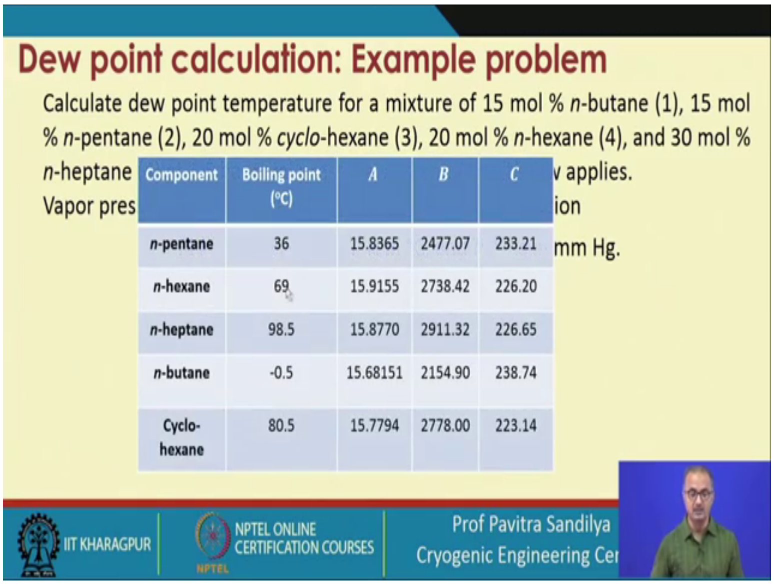

Dew point calculation: Example problem

Calculate dew point temperature for a mixture of 15 mol % *n*-butane (1), 15 mol % *n*-pentane (2), 20 mol % *cyclo*-hexane (3), 20 mol % *n*-hexane (4), and 30 mol % *n*-heptane … v applies.

Vapor pres … ion … mm Hg.

Component	Boiling point (°C)	*A*	*B*	*C*
n-pentane	36	15.8365	2477.07	233.21
n-hexane	69	15.9155	2738.42	226.20
n-heptane	98.5	15.8770	2911.32	226.65
n-butane	-0.5	15.68151	2154.90	238.74
Cyclo-hexane	80.5	15.7794	2778.00	223.14

And these are the constants which are required to find out the vapour pressure of the various components and these are the boiling points of each of the components.

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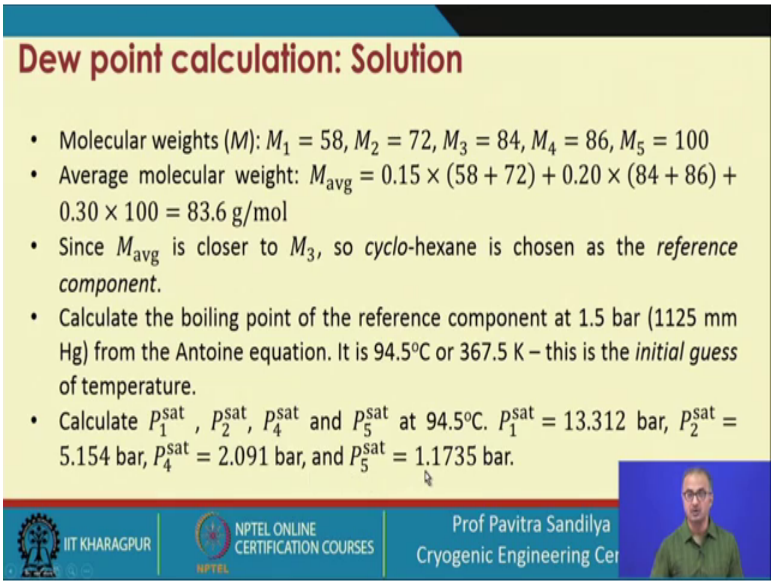

Dew point calculation: Solution

- Molecular weights (M): $M_1 = 58$, $M_2 = 72$, $M_3 = 84$, $M_4 = 86$, $M_5 = 100$
- Average molecular weight: $M_{avg} = 0.15 \times (58 + 72) + 0.20 \times (84 + 86) + 0.30 \times 100 = 83.6$ g/mol
- Since M_{avg} is closer to M_3, so *cyclo*-hexane is chosen as the *reference component*.
- Calculate the boiling point of the reference component at 1.5 bar (1125 mm Hg) from the Antoine equation. It is 94.5°C or 367.5 K – this is the *initial guess* of temperature.
- Calculate P_1^{sat} , P_2^{sat}, P_4^{sat} and P_5^{sat} at 94.5°C. $P_1^{sat} = 13.312$ bar, $P_2^{sat} = 5.154$ bar, $P_4^{sat} = 2.091$ bar, and $P_5^{sat} = 1.1735$ bar.

Now, what we do? We again find out the molecular weight of each of the components and from that we find out average molecular weight of the mixture which is coming on to 83.6 and we find here that these value is coming closer to this particular value. So, we again in this case we chose cyclo hexane as our reference component.

And once we have chosen this reference component what we do? From the Antoine equation what we do that we find out the boiling point of cyclo hexane at 1.5 bar which is coming out to be 94.5 degree centigrade or 367.5 Kelvin. So, this is our initial guess for the Dew point temperature. And from this we find out the values of the vapour pressures of the rest of the components at this 94.5 degree centigrade. And we find these are the values of the vapour pressures of the various components from the Antoine equation.

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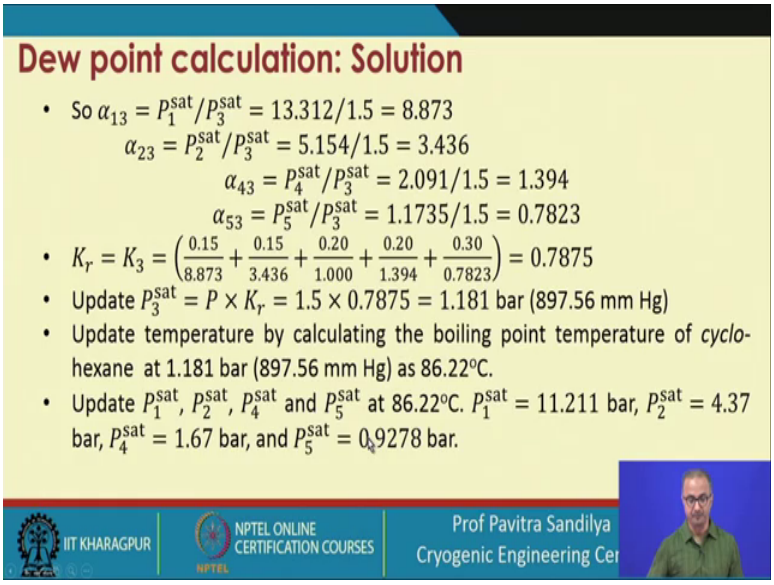

Dew point calculation: Solution

- So $\alpha_{13} = P_1^{sat}/P_3^{sat} = 13.312/1.5 = 8.873$
  $\alpha_{23} = P_2^{sat}/P_3^{sat} = 5.154/1.5 = 3.436$
  $\alpha_{43} = P_4^{sat}/P_3^{sat} = 2.091/1.5 = 1.394$
  $\alpha_{53} = P_5^{sat}/P_3^{sat} = 1.1735/1.5 = 0.7823$
- $K_r = K_3 = \left(\frac{0.15}{8.873} + \frac{0.15}{3.436} + \frac{0.20}{1.000} + \frac{0.20}{1.394} + \frac{0.30}{0.7823}\right) = 0.7875$
- Update $P_3^{sat} = P \times K_r = 1.5 \times 0.7875 = 1.181$ bar (897.56 mm Hg)
- Update temperature by calculating the boiling point temperature of *cyclo-hexane* at 1.181 bar (897.56 mm Hg) as 86.22°C.
- Update P_1^{sat}, P_2^{sat}, P_4^{sat} and P_5^{sat} at 86.22°C. $P_1^{sat} = 11.211$ bar, $P_2^{sat} = 4.37$ bar, $P_4^{sat} = 1.67$ bar, and $P_5^{sat} = 0.9278$ bar.

We use this vapour pressure values to find out the value of the relative volatility like this. And we find the relative volatility of all the components 1 3 2 3 4 3 and 5 3 because 3 is the reference component and these are the values of the relative volatilities. And then from this, we find the value of the K r and again we use this formula that is the summation of y i by K i. So, this summation formula we used to find out the value reference K value. And from this we update the value of the vapour pressure of the reference component like P into K r.

And we find this is the updated value of the vapour pressure. And with this vapour pressure value what we do again we go back to the antoine equation to find out the second updated temperature value by finding the boiling point of the reference component and that boiling point is coming out to be 86.2 degree centigrade. And with this updated value of the boiling point as a second guess of the temperature we find out the values of the vapour pressures of each of the rest of the components. And we find these are the values of the vapour pressures of the components obtained from the Antoine equation.

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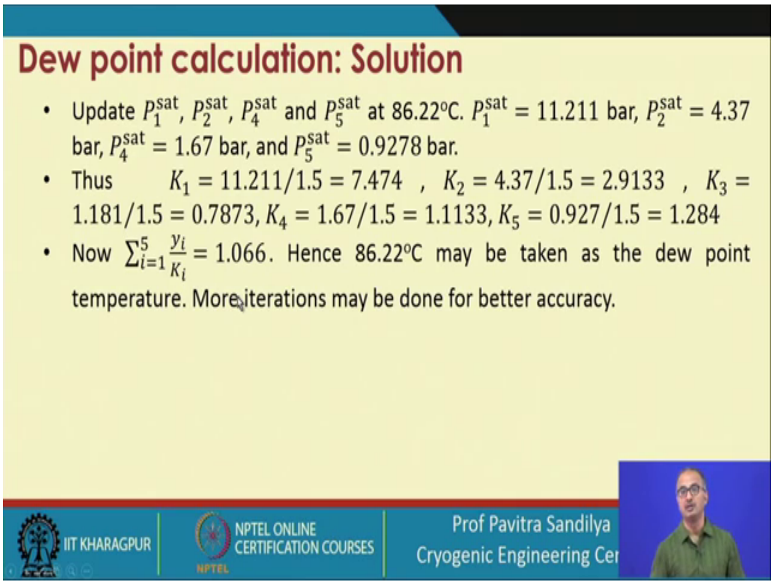

Dew point calculation: Solution

- Update P_1^{sat}, P_2^{sat}, P_4^{sat} and P_5^{sat} at 86.22°C. $P_1^{sat} = 11.211$ bar, $P_2^{sat} = 4.37$ bar, $P_4^{sat} = 1.67$ bar, and $P_5^{sat} = 0.9278$ bar.
- Thus $K_1 = 11.211/1.5 = 7.474$, $K_2 = 4.37/1.5 = 2.9133$, $K_3 = 1.181/1.5 = 0.7873$, $K_4 = 1.67/1.5 = 1.1133$, $K_5 = 0.927/1.5 = 1.284$
- Now $\sum_{i=1}^{5}\frac{y_i}{K_i} = 1.066$. Hence 86.22°C may be taken as the dew point temperature. More iterations may be done for better accuracy.

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Once we have found these then what we do that we find the values of the K 1 K 2 K 3 K 4 etcetera. Though we find these values and we find that this particular summation we do that this summation should coming out to be one now again depending on the accuracy desired by the user we may stop or we may continue the iterations to keep updating the values of the temperature. So, this is the procedure to find out the value of the Dew point temperature.

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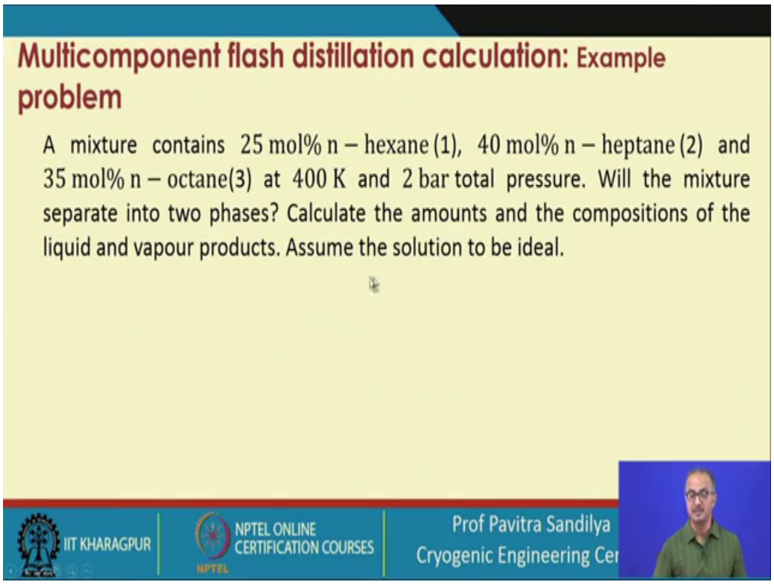

Multicomponent flash distillation calculation: Example problem

A mixture contains 25 mol% n – hexane (1), 40 mol% n – heptane (2) and 35 mol% n – octane(3) at 400 K and 2 bar total pressure. Will the mixture separate into two phases? Calculate the amounts and the compositions of the liquid and vapour products. Assume the solution to be ideal.

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In the next problem we shall be looking into the multi component flash distillation and the problem is stated like this. That we have a mixture of 20 mol percent of n hexane component 1 40 mol percent on n heptanes, component 2 and rest of it that is 35 mol percent of n octane that is component 3 at 400 Kelvin and two bar pressure and first figure out that whether the mixture will separate into two phase or not. And if we prove that yes it can be separated in two phases only then we can calculate the amounts and the compositions of the resulting phrases; that is liquid and vapour from this particular feed. And it has been mentioned that we may assume it the solution to be ideal.

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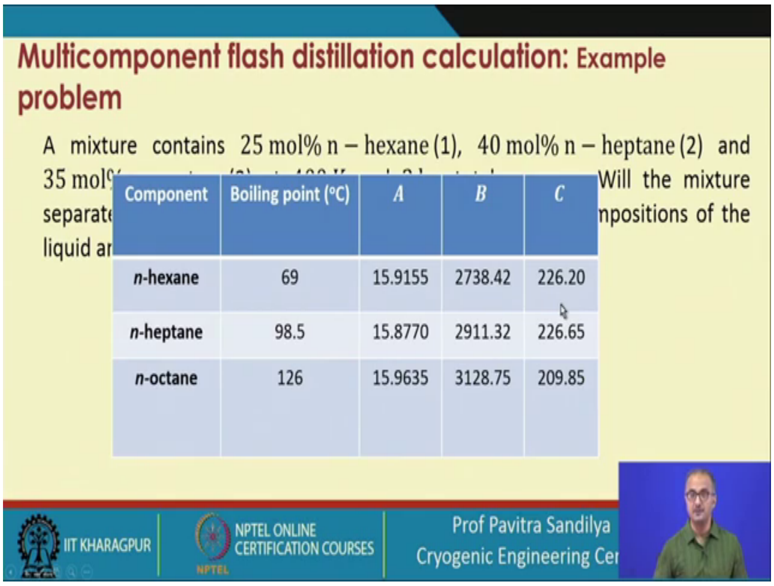

Multicomponent flash distillation calculation: Example problem

A mixture contains 25 mol% n – hexane (1), 40 mol% n – heptane (2) and 35 mol

Will the mixture

separat

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liquid ar

Component	Boiling point (°C)	*A*	*B*	*C*
n-hexane	69	15.9155	2738.42	226.20
n-heptane	98.5	15.8770	2911.32	226.65
n-octane	126	15.9635	3128.75	209.85

And once we say that then again we will be using the Antoine equation and we just list out the values of the A B C for the Antoine coefficients.

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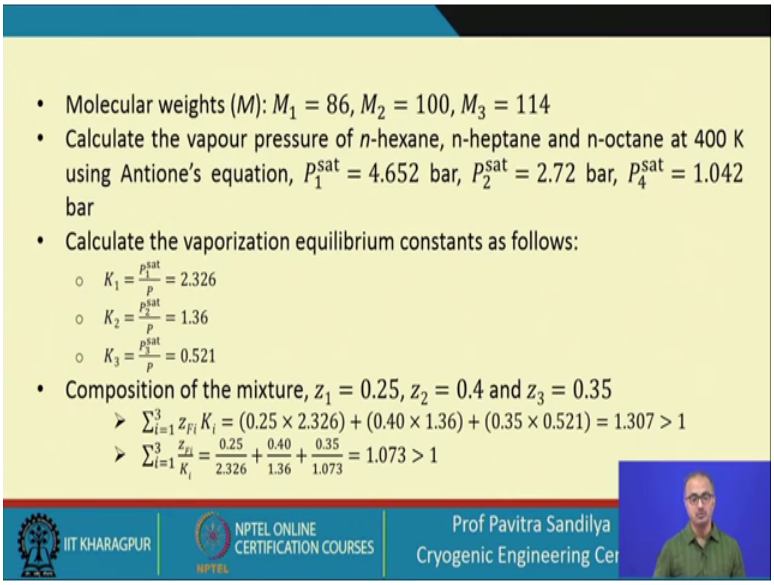

- Molecular weights (M): $M_1 = 86, M_2 = 100, M_3 = 114$
- Calculate the vapour pressure of *n*-hexane, n-heptane and n-octane at 400 K using Antione's equation, $P_1^{sat} = 4.652$ bar, $P_2^{sat} = 2.72$ bar, $P_4^{sat} = 1.042$ bar
- Calculate the vaporization equilibrium constants as follows:
    - $K_1 = \frac{P_1^{sat}}{P} = 2.326$
    - $K_2 = \frac{P_2^{sat}}{P} = 1.36$
    - $K_3 = \frac{P_3^{sat}}{P} = 0.521$
- Composition of the mixture, $z_1 = 0.25$, $z_2 = 0.4$ and $z_3 = 0.35$
    - $\sum_{i=1}^{3} z_{Fi} K_i = (0.25 \times 2.326) + (0.40 \times 1.36) + (0.35 \times 0.521) = 1.307 > 1$
    - $\sum_{i=1}^{3} \frac{z_{Fi}}{K_i} = \frac{0.25}{2.326} + \frac{0.40}{1.36} + \frac{0.35}{1.073} = 1.073 > 1$

Now going to a solution. We find again the molecular weight and the because we have been given the temperature. So, we can directly find out the vapour pressures of each of the components and these vapour pressure values will be taken to find out the key values of each of the components. And once we find the K values we what we do that these are the composition of the feed and we have been told that we if we find this K i into z f i summation and z f i by K i summation we take the summations and we were told that if these two are coming out to be more than unity then we can say that the phases will be splitting into two phases.

That means feed is split into two phases. So, these two conditions must be satisfied simultaneously to ensure that the feed splits into two phases.

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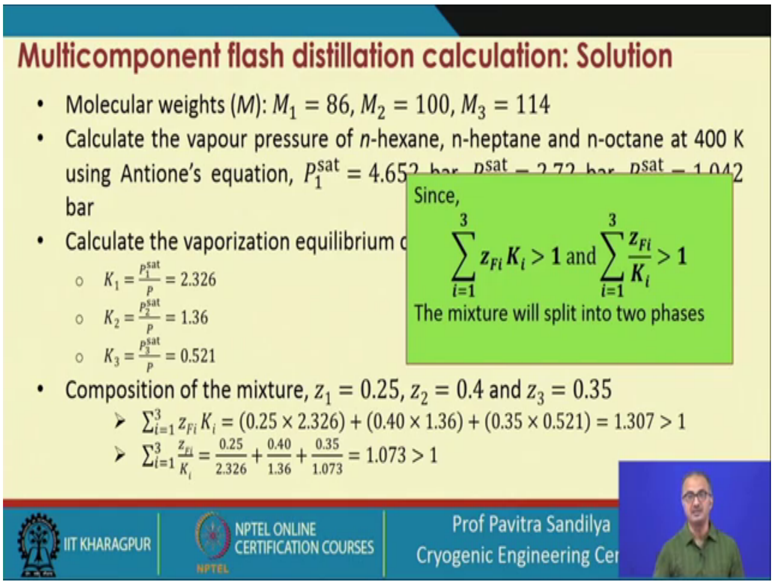

Multicomponent flash distillation calculation: Solution

- Molecular weights (M): $M_1 = 86, M_2 = 100, M_3 = 114$
- Calculate the vapour pressure of *n*-hexane, n-heptane and n-octane at 400 K using Antione's equation, $P_1^{sat} = 4.652$ bar, $P^{sat} = 2.72$ bar, $P^{sat} = 1.042$ bar
- Calculate the vaporization equilibrium c
  - $K_1 = \frac{P_1^{sat}}{P} = 2.326$
  - $K_2 = \frac{P_2^{sat}}{P} = 1.36$
  - $K_3 = \frac{P_3^{sat}}{P} = 0.521$
- Composition of the mixture, $z_1 = 0.25$, $z_2 = 0.4$ and $z_3 = 0.35$
  - $\sum_{i=1}^{3} z_{Fi} K_i = (0.25 \times 2.326) + (0.40 \times 1.36) + (0.35 \times 0.521) = 1.307 > 1$
  - $\sum_{i=1}^{3} \frac{z_{Fi}}{K_i} = \frac{0.25}{2.326} + \frac{0.40}{1.36} + \frac{0.35}{1.073} = 1.073 > 1$

Since,

$$\sum_{i=1}^{3} z_{Fi} K_i > 1 \text{ and } \sum_{i=1}^{3} \frac{z_{Fi}}{K_i} > 1$$

The mixture will split into two phases

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So, after ensuring that the feed is going into two phases what, now we are ready to do the rest of the flash calculations for this.

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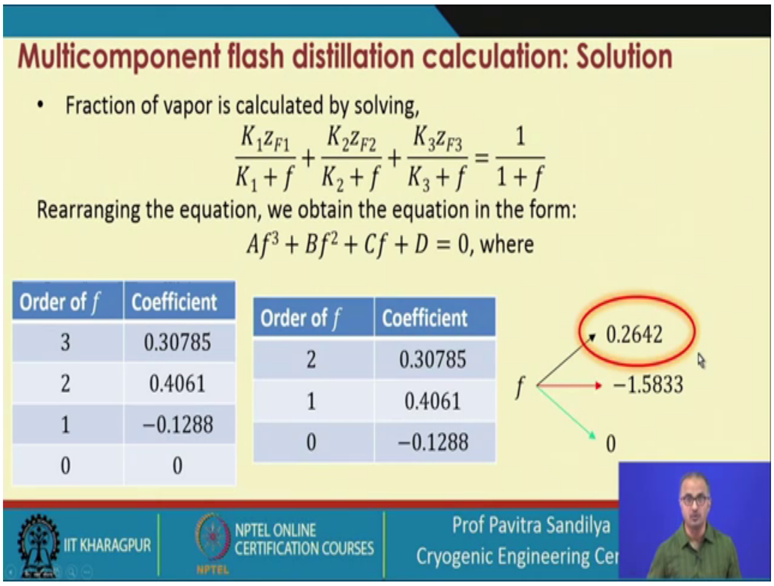

Multicomponent flash distillation calculation: Solution

- Fraction of vapor is calculated by solving,

$$\frac{K_1 z_{F1}}{K_1 + f} + \frac{K_2 z_{F2}}{K_2 + f} + \frac{K_3 z_{F3}}{K_3 + f} = \frac{1}{1 + f}$$

Rearranging the equation, we obtain the equation in the form:

$$Af^3 + Bf^2 + Cf + D = 0, \text{ where}$$

Order of f	Coefficient
3	0.30785
2	0.4061
1	−0.1288
0	0

Order of f	Coefficient
2	0.30785
1	0.4061
0	−0.1288

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What we do first we find out from this particular equation we derived earlier we use this equation which is coming from the material balance and the equilibrium relationship. And here we know that the f represents the ratio of the liquid to vapour flow rates.

And we rearrange equation and we get if we rearranged it we will get a cubic equation like this and you will find in this cubic equation you can easily find out the values of this

A B C D etcetera will be coming out to be like this. Now we find here that it is the three means like if a for this is a A value this is the B value that is the f square and f will be the this value this C and D means f to the power 0. That means, without any power to f we find this is the value of d now once we find the value of b is coming out to be 0 then we can easily see that f equal 0, 0 will be one of the solutions of this particular equation ok.

So, but f equal to 0 is not acceptable that means, that would mean that there is no splitting of the feed. So, we will not accept f equal to 0 has our solution. So, what we find that we reduce the order of the equation by one and it becomes a quadratic equation and this quadratic equation can be solved easily one of the things is 0 which is discarded and other two roots are coming out to be one positive and other is negative now negative root is not acceptable. So, it has to be positive root. So, the only solution for this one is 0.2642 that is the positive root.

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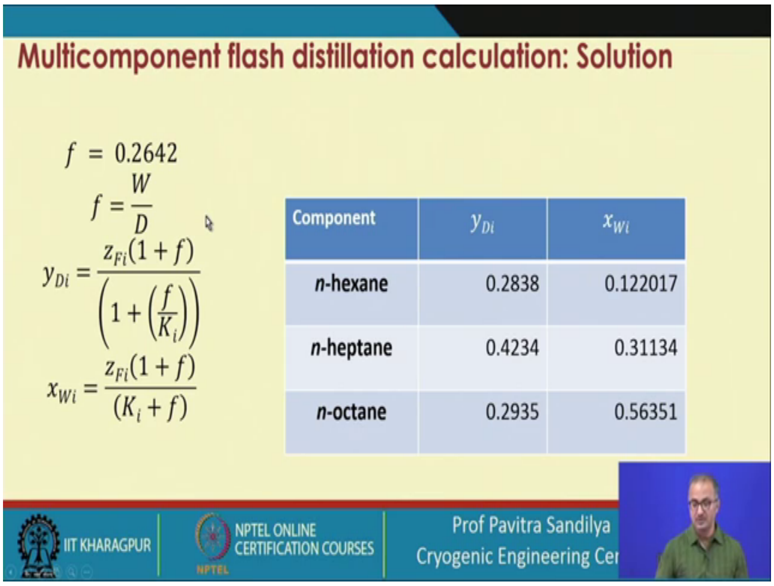

Multicomponent flash distillation calculation: Solution

$$f = 0.2642$$

$$f = \frac{W}{D}$$

$$y_{Di} = \frac{z_{Fi}(1+f)}{\left(1+\left(\frac{f}{K_i}\right)\right)}$$

$$x_{Wi} = \frac{z_{Fi}(1+f)}{(K_i+f)}$$

Component	y_{Di}	x_{Wi}
n-hexane	0.2838	0.122017
n-heptane	0.4234	0.31134
n-octane	0.2935	0.56351

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Now, once we know the value of the f then we can easily solve for the rest of the things this F as I told you this ratio of the liquid to the vapour flow rates and then we use this formula for finding out the vapour composition and a liquid composition and once we plug in the values of F and the z F i and we find these are the values of the vapour mol fractions and the liquid mol fractions of this components.

So, this is how we are able to find out the ratio of the flow rates of the vapour and liquid and also the compositions. And this problem may be extended also to know the say vapour flow rate or the liquid flow rate or both of them if we specify one of the components ok. So, this is how we are going to solve the flash problem.

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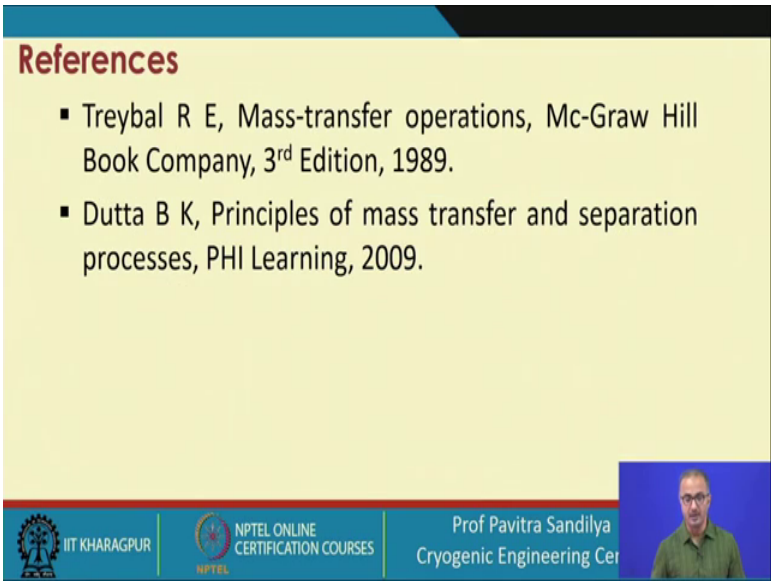

References

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

More can be known from these reference books.

Thank you.