Upstream LNG Technology
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Lecture – 05
Mixture Phase Behavior

Welcome back. Now, we shall be studying about the face behavior of a mixture of components. This is following the earlier topic; on the face behavior of the pure components. What we shall learn in this particular lecture?

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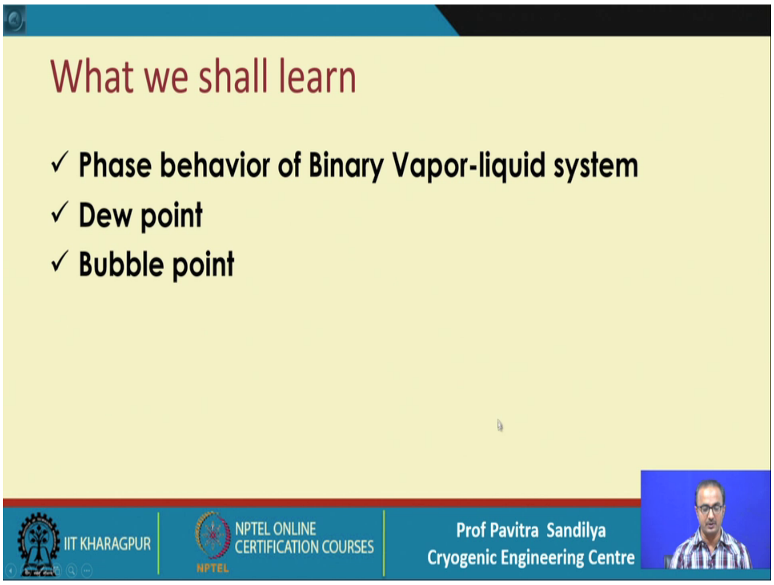

What we shall learn

- ✓ Phase behavior of Binary Vapor-liquid system
- ✓ Dew point
- ✓ Bubble point

We shall learn about the phase behavior of the binary vapor liquid systems; the dew point, the bubble point.

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- ✓ **Temperature - Composition diagram**
- ✓ **Pressure - Composition diagram**
- ✓ **Enthalpy - Composition diagram**
- ✓ **Vapor-liquid Composition diagram**

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And we shall be seeing that how we can represent the phase behavior for this binary systems. Why we are talking of binary systems? Because the multi component system phase behavior cannot be represented in 2 dimension.

So, whatever concepts we are learning for the binary systems are applicable for the multi component systems. So, in this we have temperature composition diagram, pressure composition diagram, enthalpy composition diagram and the vapor liquid composition diagram. We shall be talking about each of these diagrams one by one.

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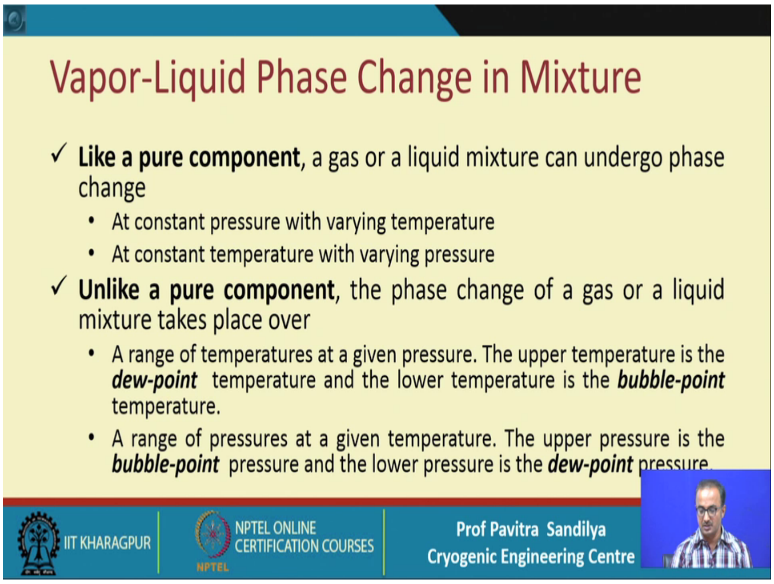

Vapor-Liquid Phase Change in Mixture

- ✓ **Like a pure component**, a gas or a liquid mixture can undergo phase change
  - At constant pressure with varying temperature
  - At constant temperature with varying pressure
- ✓ **Unlike a pure component**, the phase change of a gas or a liquid mixture takes place over
  - A range of temperatures at a given pressure. The upper temperature is the ***dew-point*** temperature and the lower temperature is the ***bubble-point*** temperature.
  - A range of pressures at a given temperature. The upper pressure is the ***bubble-point*** pressure and the lower pressure is the ***dew-point*** pressure.

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So, first let us see the vapor liquid phase change behavior in a mixture. This mixture phase change behavior is different from the phase change behavior of a pure component. Now, let us see what are the similarities and what are the dissimilarities between the phase change behavior. Now, like a pure component a gas or a liquid mixture can undergo phase change at constant pressure with varying temperature and also at constant temperature with varying pressure, but after this there are the differences, the difference is this that unlike a pure component.

The phase change of a gas or a liquid takes place over a range of temperatures at a given pressure and the upper temperature is the dew point temperature and the load temperature is the bubble point temperature; that means, the dew point temperature defines the upper temperature at a given pressure up to which we can have the liquid. And vapor phase coexisting and the bubble point temperature will be representing the lower temperature at a given pressure, at which the two phases can coexist. Similarly, the there is a limit of the pressure to at a given temperature, we have the upper pressure as the bubble point pressure and the lower pressure, the dew point pressure.

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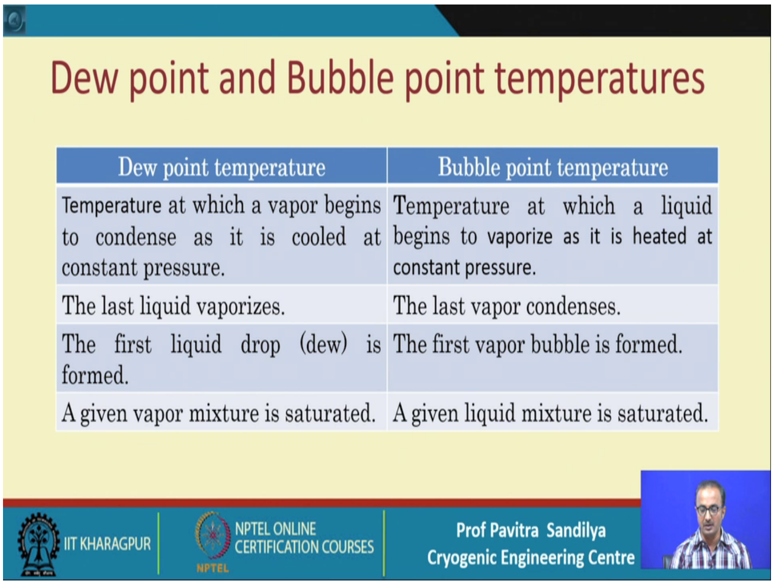

Dew point and Bubble point temperatures

Dew point temperature	Bubble point temperature
Temperature at which a vapor begins to condense as it is cooled at constant pressure.	Temperature at which a liquid begins to vaporize as it is heated at constant pressure.
The last liquid vaporizes.	The last vapor condenses.
The first liquid drop (dew) is formed.	The first vapor bubble is formed.
A given vapor mixture is saturated.	A given liquid mixture is saturated.

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Now, let us see that what are dew point temperature and bubble point temperature. Dew point temperature is defined as the temperature at which a vapor starts condensing when it is cooled at a constant pressure and bubble point temperature is defined as the temperature at which a liquid forms, the first bubble or start vaporizing as it is heated at a constant pressure. So, both dew vapor and bubble point are representing the first point, at which a particular phase is going to the next phase. Now, at the dew point temperature, we say the last liquid vaporizes whereas, for the bubble point temperature, the last drop vapor condenses and the first liquid drop or what we call dew is formed at the dew point temperature and that is how the name has been derived dew.

Thus, this is the same dew as defined in our day to day life, when we talk about the dew are forming on the grass at the night, the same thing that the temperature decreases at a given pressure. So, that the water vapor condenses on the grass and as the sun rises, again the system gets heated up and the dew goes back to the atmosphere. So, we do not find the dew in the daytime.

Similarly, for bubble point temperature the first bubble gets formed at a given pressure and a given vapor mixture is saturated at the dew point temperature whereas, the a given liquid mixture is saturated at the bubble point temperature. So, unlike a pure component, where we find that both the vapor and the liquid remains saturated at a given temperature, that is the boiling point. A case of a mixture the two section points are different.

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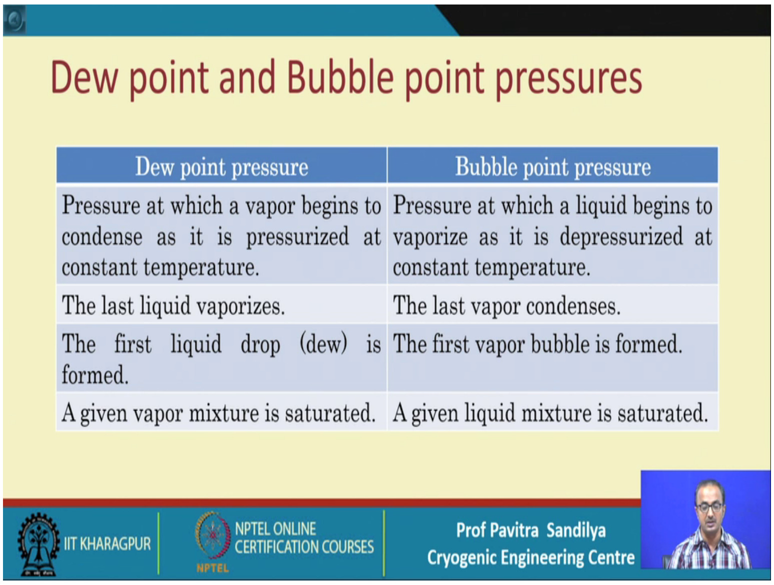

Dew point and Bubble point pressures

Dew point pressure	Bubble point pressure
Pressure at which a vapor begins to condense as it is pressurized at constant temperature.	Pressure at which a liquid begins to vaporize as it is depressurized at constant temperature.
The last liquid vaporizes.	The last vapor condenses.
The first liquid drop (dew) is formed.	The first vapor bubble is formed.
A given vapor mixture is saturated.	A given liquid mixture is saturated.

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Now, we come to the definitions of the dew point and bubble point pressures. What is dew point pressure? The pressure at which a vapor begins to condense as it is pressurized at a constant temperature and the bubble point pressure is the pressure at which a liquid starts vaporizing as it is deep pressurized at a constant temperature; that means, the whole process is being carried out isothermally as with the dew point temperature, bubble point temperature. Here, also we have the last liquid drop vaporizes at the dew point pressure whereas, the last vapor condenses at the bubble point pressure and the first liquid drop forms at the dew point pressure at a given temperature. And similarly, the first vapor bubble is forms at the bubble point pressure at a given temperature and a given vapor mixture is saturated at dew point temperature pressure and a given liquid mixture is saturated at bubble point pressure.

So, it is these definitions of the dew point temperature; dew point pressure, bubble point temperature, bubble point pressure are given with respect to the various temperature or pressures and we find that they are differing and for pure components. We can say that thus, dew point or and bubble point they merge, they merge and that point is called the boiling point temperature. So, we never talk of boiling point in case of a mixture of components.

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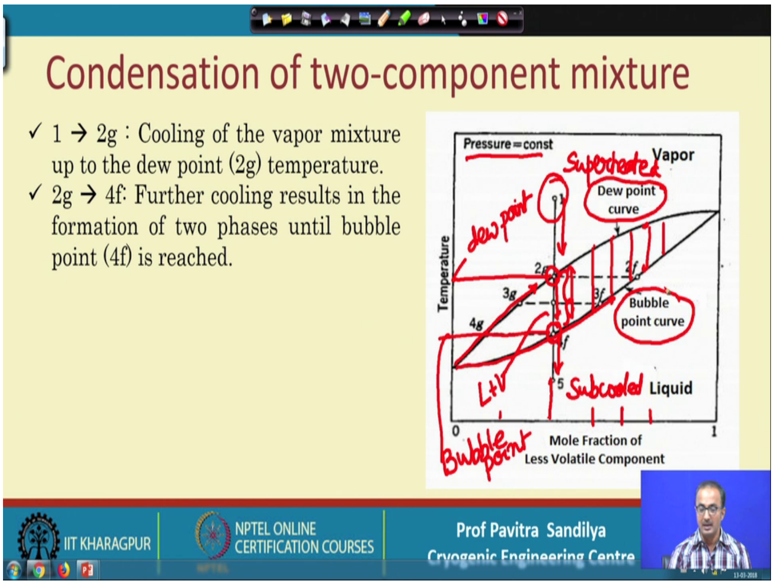

Condensation of two-component mixture

- ✓ 1 → 2g : Cooling of the vapor mixture up to the dew point (2g) temperature.
- ✓ 2g → 4f: Further cooling results in the formation of two phases until bubble point (4f) is reached.

Now, let us see the condensation of a two component mixture to component systems are also called binary systems; Now, in this let us see that what is happening that when we are plotting the temperature and the mole fraction of the components here, we see that. Suppose, we start with a vapor that is at, it is a certain composition, we start with a vapor. Now, here we see that let us start with a given composition, if we start with a given composition that is represented for 5 and 1 same and let us start with say the vapor state initially.

Now, we find in this figure that as this particular diagram has been made for a given pressure the pressure is remaining constant, all throughout the process. Now, suppose we start from the point one that is the superheated vapor and as we keep decreasing the pressure at constant, we decreasing temperature at constant pressure. We find at certain point 2 g, the first drop of liquid is formed and this 2 g point the, the temperature corresponding to this is the dew point temperature.

Afterwards as we still cool it down further, we find. We have the liquid and vapor mixture still further cooling down. We reach a point that is 4 f. We find that at this 4 f, if is now slightly cooled down, the thing it will now go to a fully liquid state; that means, starting with a superheated vapor state, we go to a sub cooled liquid state by passing through a region of liquid and vapor up to this. This is similar to a pure component behavior, the only difference comes is this. The temperature keeps varying within this two phase region, which does not happen in case of the pure component.

So, we find this temperature corresponding to 4 f is the bubble point temperature that is how the dew point is the maximum temperature and the bubble point is the minimum temperature for the existence of the liquid and vapor phases together. Now, if we carry out this experiment for different compositions I can take any composition ok. I can any composition then I use find, I will get different dew point and bubble point for each composition. So, this we can give with some straight lines. So, these straight lines are, joining the dew point and bubble point temperatures for a given composition at a given pressure.

Now, once we get all this then if I join all the dew point temperatures, we get this curve. This is called, called the dew point curve and if we join all the bubble point temperatures, we get another curve; this is called the bubble point curve. So, in your cells, the dew point curve is the locus of all the dew point temperatures at a given pressure. Similarly, the bubble point curve is the locus of the bubble point temperatures at a given pressure; in this case we find that is a significant effect of the pressure on this dew point and bubble point behavior. It has been found that as we increase the pressure the difference between the dew point and bubble point comes down; that means, we increase the pressure we find these two curves will start coming closer and closer at higher pressure.

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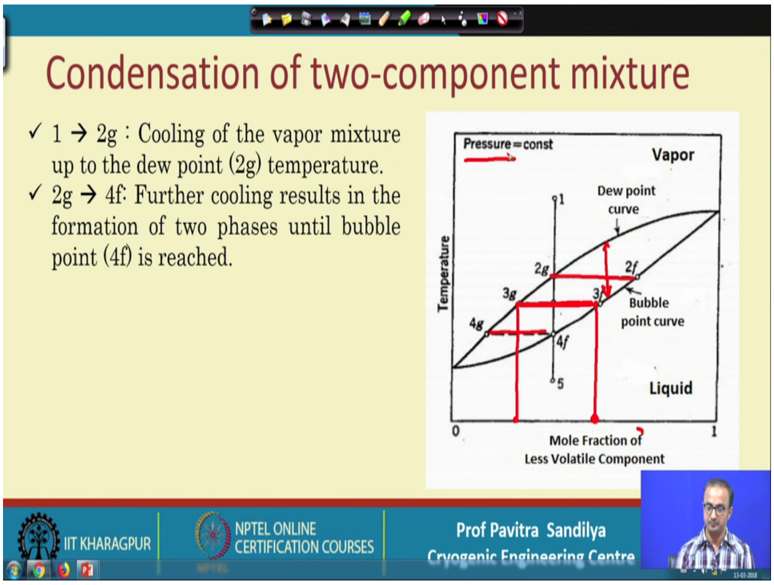

Condensation of two-component mixture

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So, with this knowledge of the temperature and the composition, we can find out that how we can get the various types of separations in case of a mixture of components, when we are cooling the mixture. For example, natural gas at a given pressure, and in this figure if I look at any of these horizontal lines; that is this particular line represents a constant, constant temperature region.

And wherever it is intersecting with the dew point curve and the bubble point curve, corresponding to dew point curve, we get the composition of the species in a liquid phase and corresponding to the, this point, which is intersecting with the bubble point curve. We get the composition of the same species in the vapor state, at the particular temperature and at a given pressure.

So, we can know the composition vary variation in the two phases for a given mixture of liquid, the mixture with variation of the temperature between the dew point temperature and the bubble point temperature, we shall be learning about the ways to determine the dew point temperature, bubble point temperature, etcetera later on. Next, we come to the representation of the pressure composition diagram.

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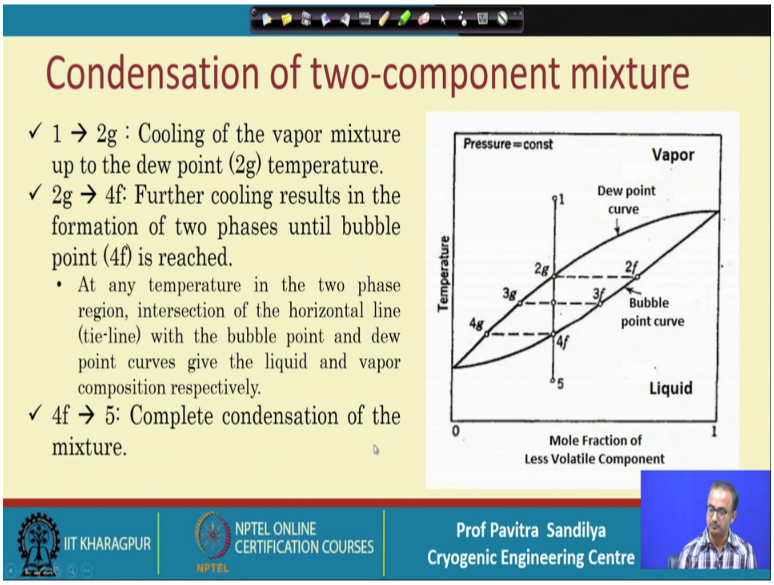

Condensation of two-component mixture

- ✓ 1 → 2g : Cooling of the vapor mixture up to the dew point (2g) temperature.
- ✓ 2g → 4f: Further cooling results in the formation of two phases until bubble point (4f) is reached.
  - At any temperature in the two phase region, intersection of the horizontal line (tie-line) with the bubble point and dew point curves give the liquid and vapor composition respectively.
- ✓ 4f → 5: Complete condensation of the mixture.

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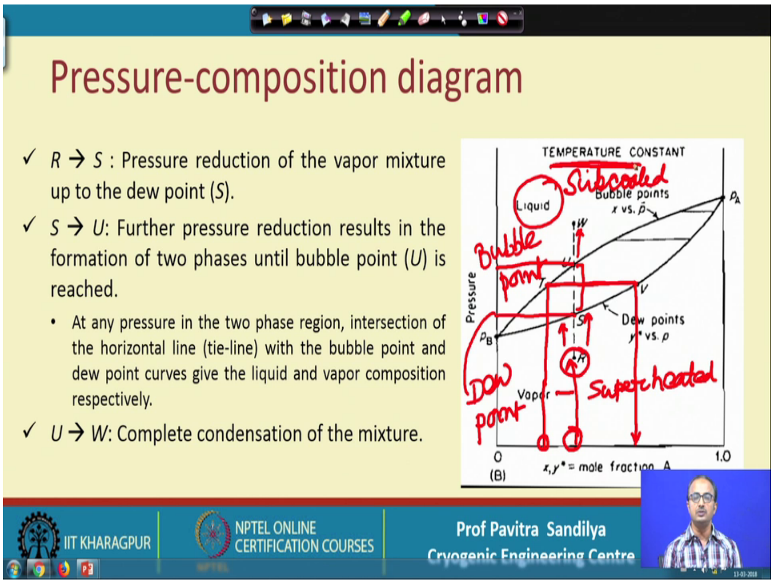

Pressure-composition diagram

- ✓ *R* → *S* : Pressure reduction of the vapor mixture up to the dew point (*S*).
- ✓ *S* → *U*: Further pressure reduction results in the formation of two phases until bubble point (*U*) is reached.
  - At any pressure in the two phase region, intersection of the horizontal line (tie-line) with the bubble point and dew point curves give the liquid and vapor composition respectively.
- ✓ *U* → *W*: Complete condensation of the mixture.

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Once we have understood the temperature composition diagram, this understanding of the pressure composition is also quite simple, only thing in this case we have to remember is that for the pressure system. The vapor will be existing at a lower pressure that is in case of temperature composition. The vapor was on the upper side, but in case of pressure composition, the vapor is on the lower side.

So, in this case, we start with a point R. This is a superheated vapor region and for a given composition, if we start lowering the pressure at a given temperature, temperature is constant we find that at certain point S, the first liquid do will form and this point is called the dew point pressure and on further depressurization, we find. We have the two phase region and ultimately we reach a point U, when on further depressurization pressurization.

Sorry, we get the liquid; that means, as I keep increasing the pressure. First I go to two phase regions, which starts at S, that is the dew point pressure and then we go to the bubble point pressure. And if I raise the pressure above the bubble point, we will end up with the sub cooled liquid region and this is true for a given composition and in between this two phase region again I can have a isobaric line. And in this case again we find this V point, which is intersecting with the dew point will give the liquid phase composition and this T with sorry, this give the vapor phase composition and this point will give the liquid phase composition at a, at this particular pressure and at this particular temperature.

So, that is how we can know that how the composition of the liquid and the vapor would change with the change in the pressure at a constant temperature for a given mixture. I am not specifying this about binary, because whatever concepts we are developing they are applicable for multi component systems as well. Now, again as for the temperature composition diagram, if we join all the dew point temperature, dew point pressures we get the dew point curve and if we join the bubble point, pressures, we get the bubble curve.

And in this case you can note that the dew point pressure is less than the bubble point pressure and whereas, the dew point temperature is more than the bubble point temperature. So, with this we have known, how we represent the temperature composition and vapor composition diagrams. Next, we come to another presentation and this representation is the vapor liquid composition diagram.

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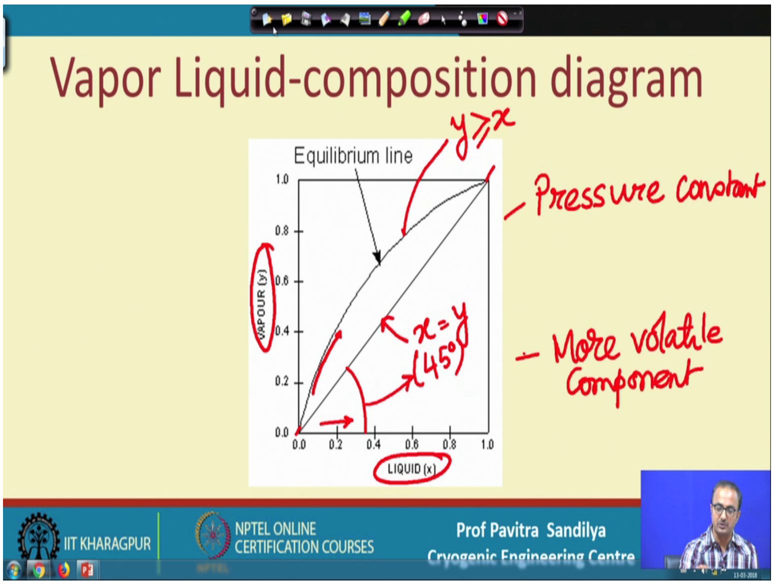

Vapor Liquid-composition diagram

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Now, in this particular diagram what we do? We are defining the composition of the vapor and liquid and for a binary systems. We know that the summation of the mole fractions or mass fractions is always unity. So, if I give the mole fraction of one component, the other components mole fraction can easily be found out by subtract and subtract a neat form from 1.

So, what we are doing here that, we are representing the composition diagram and in this, we are putting on the y axis. The vapor composition which is given in terms of y and on the x axis, we have the liquid phase composition for the, we represented by x and this is applicable for more volatile component by which I mean that the component, which can go to the vapor phase more easily; that is the more volatile component. And these particular diagrams pertains to the more volatile component and let us see that what happens, then this particular diagram is made for a given pressure, the pressure is constant.

Now, in this case we see if we refer to the temperature composition diagram, we find that as we keep increasing the temperature, We find that the y that is the vapor phase mole fraction of the more vital component will keep on increasing with an increase in the liquid phase mole fraction and this kind of bulge will be formed. This particular line is the x equal to y line ok; that means, it has a 45 degree angle. This is the 45 degree angle.

So, this particular x x or y line and we find that this particular curve between the y and x is going above the xq 2 y line, it means for this particular curve y is always more than x and at the most and the two corners will be having y is equal to x. Now, when y is more than x, it means that component has a tendency to go to the vapor phase more than staying in the liquid and this shows that this component is the more volatile component.

It is not necessary that we have to represent this kind of diagram, only in terms of the more volatile component. If somebody wants to, wants to put in terms of less volatile component, then you will, you can easily see that.

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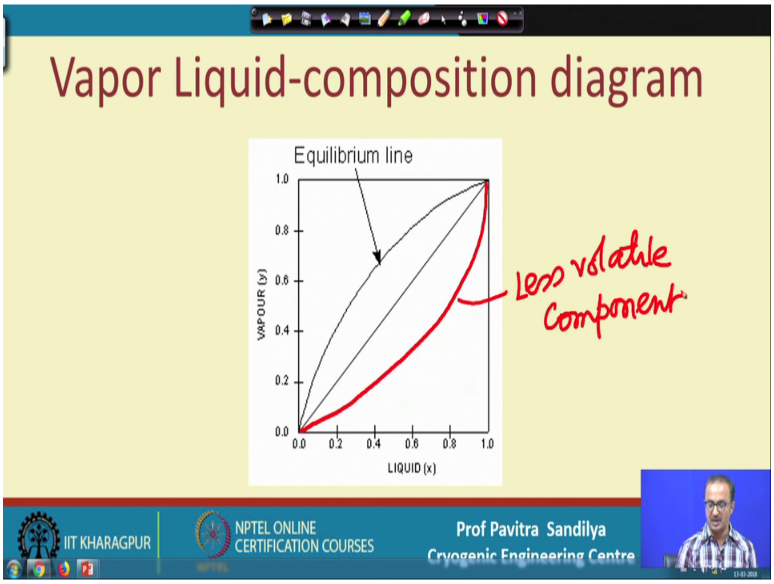

Vapor Liquid-composition diagram

It will be looking like this. So, this is for this volatile component. So, conventionally we make all these diagrams in terms of the more volatile component.

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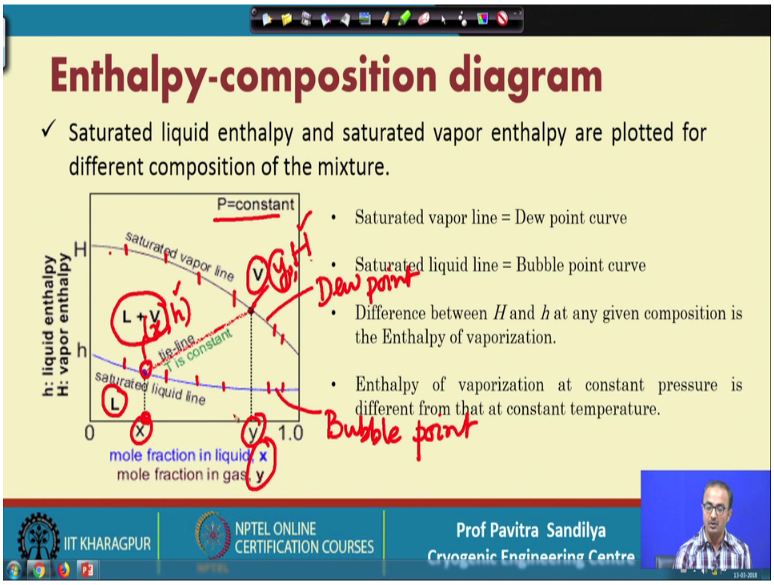

Enthalpy-composition diagram

✓ Saturated liquid enthalpy and saturated vapor enthalpy are plotted for different composition of the mixture.

- Saturated vapor line = Dew point curve
- Saturated liquid line = Bubble point curve
- Difference between H and h at any given composition is the Enthalpy of vaporization.
- Enthalpy of vaporization at constant pressure is different from that at constant temperature.

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Lastly, we come to another representation that is the enthalpy composition diagram, which is not as popular as the temperature composition of pressure composition diagrams, but still is used for some kind of analysis, in this case what we are doing that we are plotting the enthalpy of the saturated vapor and the saturated liquid. Now, in this case we know that vapor enthalpy for a given composition and pressure will always be more than the liquid enthalpy.

So, we find that for different compositions we find that we shall have with different types of saturated vapor enthalpies and corresponding to same composition. We will be having the saturated liquid enthalpies and on this x, we are putting x or y; that means, when I am reading this we shall be having the y and the vapor composition say H here.

In this case it is capital H, that capital represents the saturated vapor enthalpy and corresponding to this y, we have a another liquid phase composition that is in equilibrium and this can be obtained from the x y diagram, which we learnt earlier and corresponding to this point, we shall be having another enthalpy. This is the x versus h x is the mole fraction of the component.

In the liquid phase, which is in equilibrium with mole fraction of the same component in the vapor phase and H is the saturated liquid phase enthalpy of, at this composition and H is the saturated vapor phase enthalpy at the same composition and in this case the pressure is remaining constant.

Now, like earlier if we join all the saturated vapor phase enthalpy, we get another curve. This is the dew point curve, dew point curve and if we join the saturated liquid enthalpy, we get the bubble point curve and below this bubble points, we have only liquid sub cooled liquid and above this we have only superheated vapor. Whereas, between these two enthalpy lines, we have the mixture of the liquid and the vapor and here you can see the tie line, that tie line is the line joining the equilibrium compositions. This tie line is not vertical or horizontal. It is straight line, but it has some angle in general.

So, this time line is representing is joining the compositions at equilibrium that is x and y and this x and y on a, phase, composition diagram will represent a point. So, this way we can represent the equilibrium of a binary system in terms of the enthalpy composition diagram.

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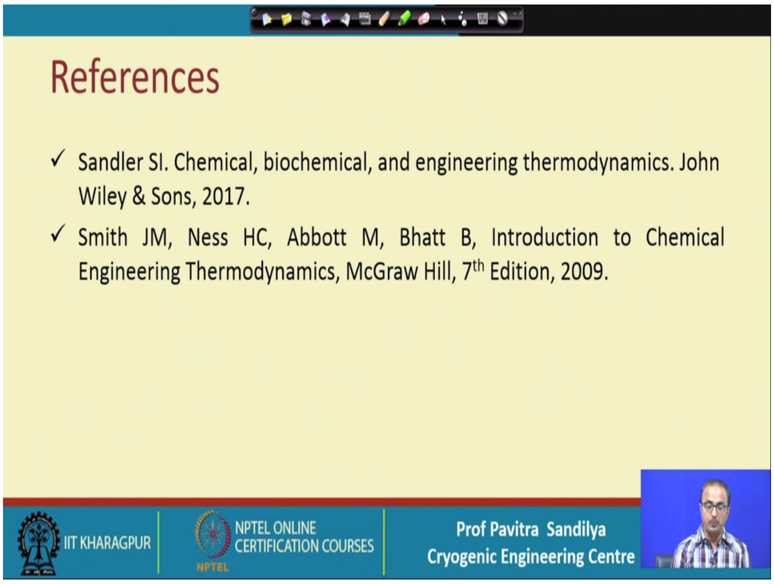

References

- ✓ Sandler SI. Chemical, biochemical, and engineering thermodynamics. John Wiley & Sons, 2017.
- ✓ Smith JM, Ness HC, Abbott M, Bhatt B, Introduction to Chemical Engineering Thermodynamics, McGraw Hill, 7th Edition, 2009.

These are, both are the Thermodynamics of phase behavior for both the pure component and the mixture of components can be found in many Thermodynamics book, related to chemical engineering. I have given the names of two books, which are quite often used as textbooks, that is one by Sandler and another by JM Smith and Van Ness. These both are very popular books in the undergraduate and postgraduate courses. You may refer to these books to know more detail and some problems on these topics.

Thank you.