

Cryogenic Engineering
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Lecture No. # 20
Gas Separation

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CRYOGENIC ENGINEERING

Earlier Lecture

- A mixture composition can be represented by either volume, mass or mole fractions.
- Work of separation is represented by $W_{i,m}/n_m$, $W_{i,m}/n_A$ and $W_{i,m}/n_B$ (for **Gas A** and **B**). Additionally, it is also represented by $W_{i,A}/n_A$, $W_{i,B}/n_B$ and $W_{i,C}/n_C$ (for **Gas A, B** and **C**).
- Ideal work of separation/mole of mixture with **N** constituents is given by
$$\frac{-W'_i}{n_m} = \Re T_m \sum_{j=1}^N y_j \ln \left(\frac{1}{y_j} \right)$$
- where y_j is mole fraction of **jth** component.

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So, welcome to that 20 th lecture of cryogenic engineering under the NPTEL program. In the earlier lecture on cryogenic engineering, we are talking about Gas separation and we are going to continue talking on Gas separation. A mixture composition can be represented by either volume, mass or molar basis molar fractions this is what we did, this is what we understood in the last two lectures. Then we found out the expression for work of separation and this work of separation is represented by $W_{i,m}$ by n_m , that is work of separation of mixture, ideal separation; ideal work of separation of mixture per mole of mixture.

Similarly, the ideal work of separation of mixture per mole of Gas A or similarly, per mole of Gas B, when a mixture is made up of Gas A and Gas B. Additionally, it is also represented by work of separation of a only from A mixture of A and B per mole of a or work of separation of B only per mole of B or work of separation of C only per mole of C, for a mixture of Gas A, Gas B and Gas C.

So, there are two possibilities, three possibilities, three component mixture possibilities, there could be n number of components in a mixture. This n number of components can all be separated at one time or only one component can be separated at out of this n components. And a work of separation of this one component from mixture is different; then work of separation of all the components of the mixture at the same time is different. This what we have seen last time, we also solve some tutorial problem to understand the values associated with this.

The idea work of separation per mole of mixture with N constituents is given by this formula. We had studied the derivation of this formula at the same time we solved some problem to understand, what is a relevance or what is the significant of this formula in order to get ideal work of separation per mole of mixture, per mole of Gas A, per mole of Gas B or per mole of Gas C. So, it is $R T_m \ln \left(\frac{1}{\sum y_j} \right)$ this is the ideal work of separation per mole of mixture, where y_j is a mole fraction of the jth component, this is what we studied last time.

Now, what is important here, we are going to talk about now, the mixture composition of different moles, different components and therefore, all this mixture are governed by some rules.

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Outline of the Lecture

Topic : Gas Separation (contd)

- Gibbs Phase Rule
- Phase Equilibrium Curves
- Temperature Composition Diagrams

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And therefore it is very important to understand this rules, there are some laws associated with this. And now, will spend some time in understanding, what are those basic rules,

basic laws which govern this mixture. From this of view, the outline of the lecture is basically, we want to try understand, what is this Gibbs phase rule? What is the phase equilibrium curves? What are the temperature composition diagram? Because the information which we get from this rules and curves and diagram is very important in order to understand the separation of different gases. And from that of view this lecture is dedicated to understand Gibbs phase rule, phase equilibrium curves and temperature composition diagram. So, a mixture can have various components and can exist in various phases in thermal equilibrium.

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CRYOGENIC ENGINEERING

Introduction

- A mixture can have various components and can exist in various phases in thermal equilibrium.
- For example, a mixture of ice and water is a 1 – component and a two phase mixture.
- If number of components and number of phases in thermal equilibrium are denoted by C and P respectively, then for above mixture $C=1$ and $P=1$
- Similarly, boiling **LAir** is **LOX + LN₂ + N₂ + O₂**, the values of C and P are 2 and 2 respectively.

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As you know, we can have different components and therefore, different phases which are in thermal equilibrium. For example, a mixture of ice and water is a 1 component and a 2 phase mixture obvious, we got a solid and liquid phase in thermal equilibrium with each other and it is only of it is a 1 component. If number of components and number phases in thermal equilibrium are denoted by C and P respectively, C is number of components and P is number of phases and then for above mixture C is equal to 1 and P is equal to 1, for a single component we can call C is equal to 1 and P is equal to 1.

Similarly, we got other possibilities of having mixture, wherein we got a boiling liquid air, boiling liquid air will have LOX; that means, liquid oxygen, liquid nitrogen, nitrogen Gas and oxygen gas. So, we got 2 components that are present in 2 phases liquid and Gas, liquid and gas. So, the values of C and P here will be 2, 2 components it is nitrogen

and oxygen and 2 phases that is liquid and Gas. Every mixture now, can be uniquely defined by a set of properties called as Thermostatic Properties.

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CRYOGENIC ENGINEERING

Introduction

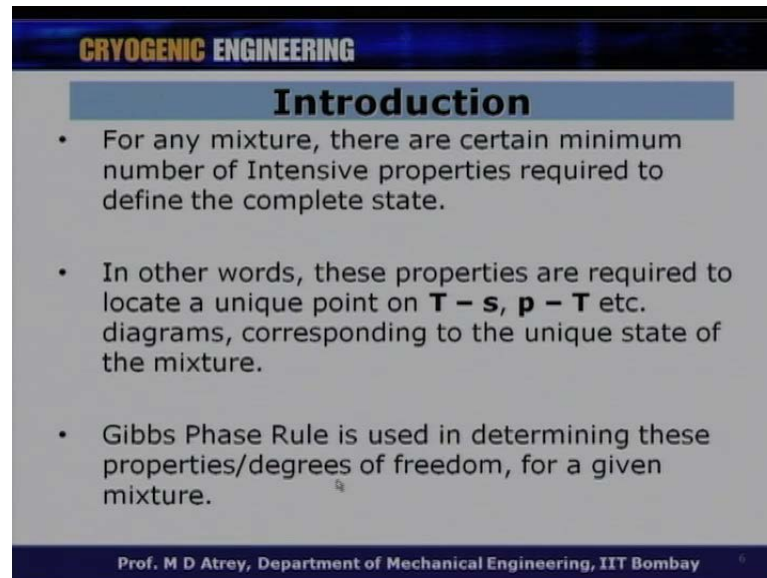
- Every mixture can be uniquely defined by a set of properties called as Thermostatic Properties.
- These properties can either be Intensive (independent of mass) or Extensive (dependent on mass) properties.
- Pressure, temperature, density are examples of Intensive properties and volume, enthalpy, entropy are few examples of Extensive properties.

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So, when we got a 2 component 1 phase 2 phase, whatever number of phases, we will have to define this mixture by some unique properties which are called as thermostatic properties. So, all this thing which were doing is basically to understand, if I want to define a particular mixture, how many property should there be in order to define that mixture. These properties can either be Intensive properties or Extensive properties, what is Intensive means? They are independent of mass, Extensive means? They depend on mass.

What are these properties? For example, pressure temperature density are examples of intensive properties, they do not depend how much mass is there. These are independents of mass properties and there are standard characteristic of a given Gas or basically, any constituent we are talking about. While volume, enthalpy, entropy are few example of extensive properties, because they will depend on what is the mass of the system. So, these parameters definitely depend on the mass and therefore, they are called extensive properties.

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CRYOGENIC ENGINEERING

Introduction

- For any mixture, there are certain minimum number of Intensive properties required to define the complete state.
- In other words, these properties are required to locate a unique point on **T - s**, **p - T** etc. diagrams, corresponding to the unique state of the mixture.
- Gibbs Phase Rule is used in determining these properties/degrees of freedom, for a given mixture.

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For example, any mixture there are certain minimum number of intensive properties normally, I would look for intensive properties in order to get all the details of an any component or any mixture. So, for any mixture, we need to have certain minimum number of intensive properties to define the complete state. In other words, these properties are required to locate a unique on a temperature entropy diagram or a pressure temperature diagram or pressure enthalpy diagram etcetera, corresponding to the unique state of the mixture. So, as soon as I know that, a mixture should have 2 or 3 properties to be known so that I can locate the properties of these mixtures they are called an important properties or they are called an intensive properties of this particular mixture.

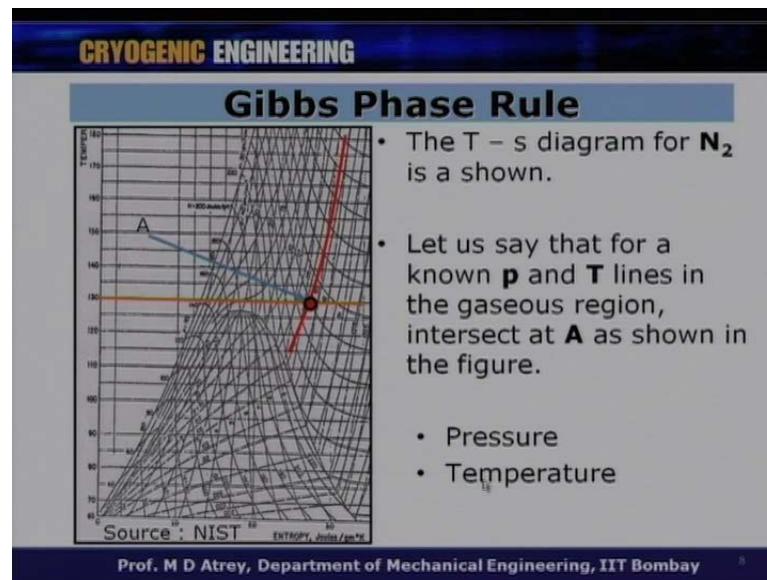
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The slide is titled "CRYOGENIC ENGINEERING" and "Gibbs Phase Rule". It contains three bullet points: 1. Gibbs Phase Rule was formulated by Josiah Willard Gibbs, an American physicist, in 1878. 2. If F is the degrees of freedom/minimum number of Intensive properties required to define the thermodynamic state of a system, then by Gibbs Phase Rule $F = C - P + 2$. 3. For example, for gaseous N_2 , we have $C = 1$ and $P = 1$. Therefore, $F = 2$. The slide footer reads "Prof. M D Atrey, Department of Mechanical Engineering, IIT Bombay" and has a small number "7" in the bottom right corner.

The Gibbs phase rule is used to determine these properties or we can call them as degrees of freedom or so, because a degree of freedom will define a particular system. So, similarly, the number of properties or degrees of freedom will define a particular mixture or a component also for a given mixture. So, how many components are there? How many phases are there? Which will decide, how many properties known to us? How many degrees of freedom known to us to define this particular mixture. So, the Gibbs phase rule was formulated by Josiah Willard Gibbs, an American physicist, in 1878 so this is a very old rule, but is a very important rule. If F is the degrees of freedom or minimum number of intensive properties required to define a thermodynamic state of a system, this is what we talked about, then the Gibbs phase rule is given as F is equal to C minus P plus 2.

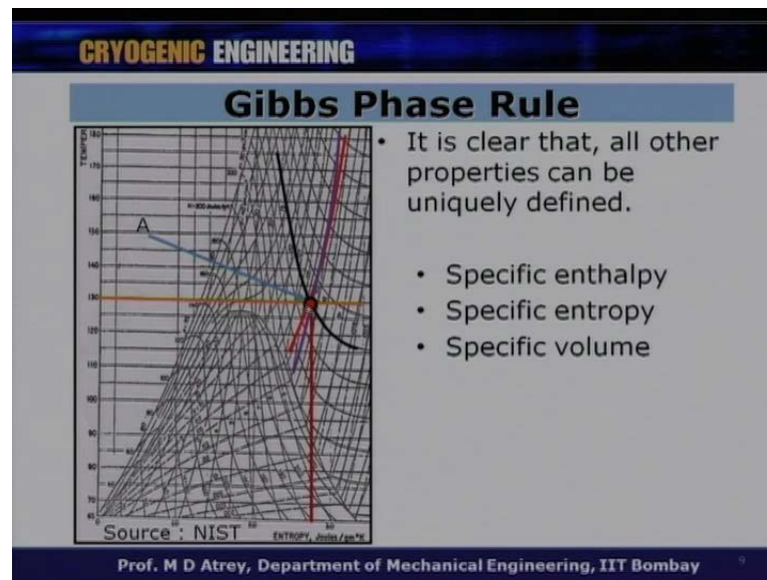
Now, many of you possibly know, what is this Gibbs phase rule? But Gibbs phase rule is a very important rule as for as cryogenic mixtures are considered and that is why I am repeating it is from basic. So, F is equal to, F is nothing but the degrees of freedom or minimum number of intensive properties, C is number of components, P is number of phases and therefore, F is equal to C minus P plus 2. Now, let us see how do we define different mixtures? For example, for gaseous nitrogen, we have C is equal to 1 that is nitrogen only, P is equal to 1 that is Gas only. And therefore, F is equal to 2; that means, we require 2 minimum properties known to us, in order to define a state of nitrogen at any given time. These can be pressure temperatures or pressure specific volume etcetera.

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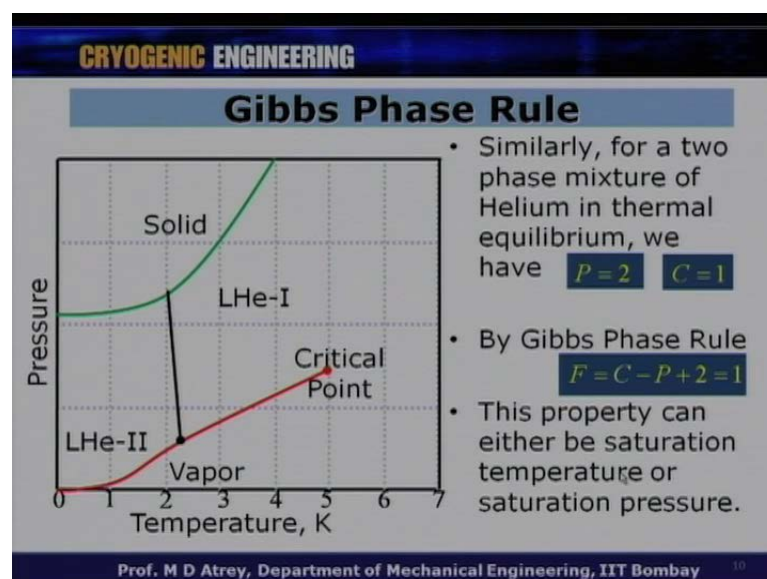
Let us see for example, on this diagram, which is a temperature entropy diagram and most of you are familiar with this temperature entropy diagram. Now, let us see that a known points are P and T this is a pressure and temperature here, I need to locate a point in the gaseous, this is a gaseous region. As you know this is a dome, inside this dome what we have is a 2 phase region, but we are talking about a single component and single phase and therefore, we are in gaseous region. And therefore, I want to locate a point in the gaseous region, what do I need to know here, in order that I locate this point A, I note to know pressure and temperature. So, if I know this two points, the intersection of this is point is a unique point and this define this point A.

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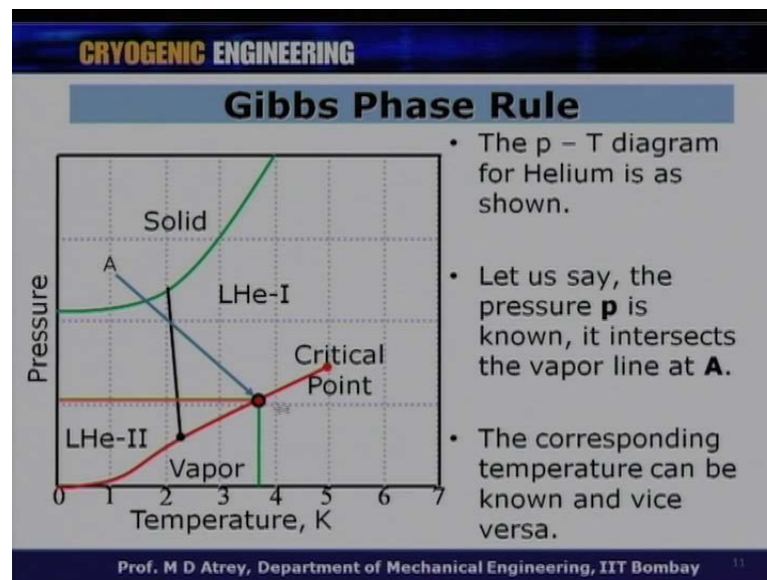
So, let us say that for a given or known P and T lines in the gaseous region, they intersect at point A as shown and they are pressure and temperature. It is clear, all other properties having known this point A , we can find all other properties of this Gas Component at point A and is a unique point now. And therefore, all the properties like specific enthalpy, specific entropy, specific volume etcetera, all this can be located from the same diagram. So, basically what is important here, to know the degrees of freedom are 2, is 2, the intensive properties or the intensive properties are required to define these component is only 2.

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Now, I got a second example. Similar, for a two phase mixture now, instead of having one phase, because two phases now. So, for a two phase mixture of, let us say Helium, this diagram is all of you know this diagram, this is a phase diagram of basically liquid Helium both the phases are in thermal equilibrium what we have. Therefore, is P is equal to 2, C is equal to 1 only component, only one which is helium, but the phases are 2, C is equal to 1. So, by Gibbs phase rule F is equal to C minus P plus 2 which will give me 1. Which means that, if I have got a two phase of Helium I will need to know only one property and once I know this property, I can locate this point, how do I know this see. This property can either be saturation temperature or saturation pressure.

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So, how can; how will I do, I got this pressure temperature diagram of helium as shown. This is a line which gives vapor and liquid in thermal equilibrium. So, if I want to locate any point, any 2 phase point which is in thermal equilibrium both the phases are in thermal equilibrium. As soon as know, I know pressure, I can locate this point on this curve. So, or even if know temperature, I can draw a vertical and I will locate this point on this vapor liquid phase diagram here, I got a vapor, I got a liquid on this side and this is nothing but a vapor pressure curve. So, if I know the vapor pressure curve, because this is a known characteristic of helium.

So, as soon as I know, one property may be pressure or may be temperature I can locate this point A. So, let us say, the pressure P is known, it intersects the vapor line at A, the

corresponding temperature can be known immediately; that means, I can calculate all the values associated this point A. Which means that I should know only 1 point or 1 degree of freedom or 1 intensive property may be pressure or temperature in order to locate this a in this phase diagram. Why, because there are 2 phases which are in thermal equilibrium with each other only 1 component.

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The slide features a blue header with the text "CRYOGENIC ENGINEERING" in yellow. Below it, a blue bar contains the title "Phase Equilibrium Curves" in white. The central part of the slide shows a diagram of a gas mixture represented by a grid of red and green circles, each containing a letter 'A' or 'B'. Below the diagram is a bulleted list of text. At the bottom of the slide, a blue footer contains the text "Prof. M D Atrey, Department of Mechanical Engineering, IIT Bombay" and a small logo.

- Again, for a mixture of **Gas A** and **Gas B** in single phase, we have $P = 1$ and $C = 2$.
- Using the Gibbs Phase Rule, $F = 3$
- These properties are pressure, temperature and mole fraction of one of the components.

So, this gives me, the second part now, let us come to the phase equilibrium curve and I got a mixture of A and B. And again, for a mixture Gas A and Gas B. Now, there are two components till now, we are talking about only one component, but if I got two components Gas A and Gas B, I got C is equal to 2 now, I got P is equal to 1 in this case. So, they are both of them are in gaseous state therefore, P is equal to 1, C is equal to 2 by using Gibbs phase rule, I now have a F is equal to 3; that means, I should know 3 properties intensive properties or degrees of freedom of 3.

So, what are these properties? These properties are pressure temperature, this is what we had for single phase, in addition to that, we have got to have a mole fraction of one of the components. So, when you have got a two components mixture, both of them in the same phase, which is Gas phase, I should have three properties to be known to me in order to locate and they are pressure temperature and mole fraction of one of the components. This will give me all the properties associated with this Gas mixture and this is very important.

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CRYOGENIC ENGINEERING

Phase Equilibrium Curves

- In general, phase of a 1 – component system is governed by pressure and temperature.
- But for a 2 – component mixture at a given pressure, the mole fractions of components in vapor and liquid phases change with the temperature.
- Variation of mole fraction (**y**) with temperature (**T**) at a constant pressure (**p**) is given by **Temperature composition diagram** or **Phase – equilibrium curve**. 3 typical curves are explained in further slides.

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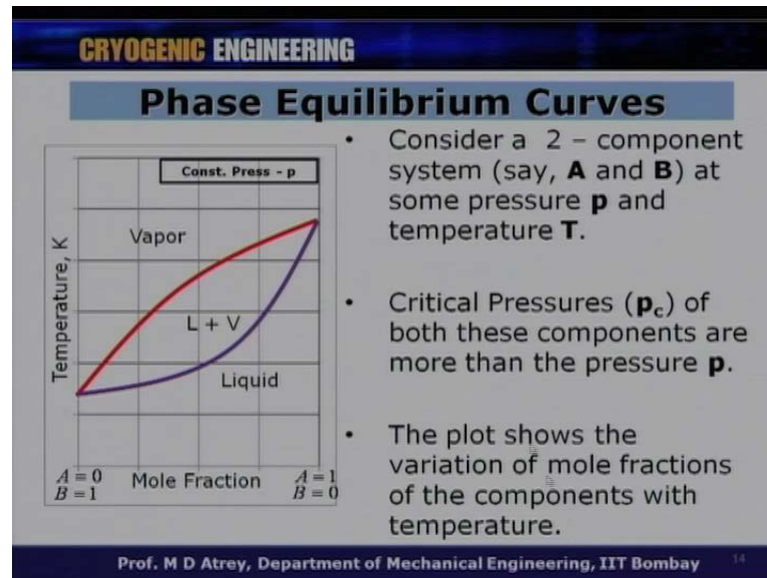
In general, phase of 1 component system is governed by pressure and temperature. But for a 2 component mixture at a given pressure, the mole fractions of the components in vapor and liquid phases change with the temperature and that is why we need to have a molar fraction, the third property. The 2 component mixture at a given pressure the molar fraction of component in vapor and liquid phases change with temperature and therefore, we need to know this molar fraction.

So, variation of this mole fraction Y with temperature T is what is given by temperature composition diagram or a phase equilibrium curve. So, this is what we basically are going to now. This we just found that for a 2 component mixture, we should know temperature pressure and molar fraction. And this is what is given by a temperature composition diagram or P versus mole fraction, T versus mole fraction for a given pressure and this is exactly what we want to study now, for mixtures which is temperature composition diagram or phase equilibrium curve.

There are 3 typical curves of which I will explain to you in next slides. So, basically have understood now, I need to know 3 components and this 3 component I can understand from temperature composition diagram. So, this is a typical temperature composition diagram which will come across. So, there are 2 components, considered 2 component system A and B. So, here I got A is equal to 0; that means, B is equal to 1, on the X axis I am plotting basically mole fraction, on the Y axis I have got temperature and this curve

is given for a constant pressure p we will go in detail of this diagram, but what you can understand here this is a is equal to 0 and a is equal to 1; that means, in this direction a increases and in the opposite direction b decreases.

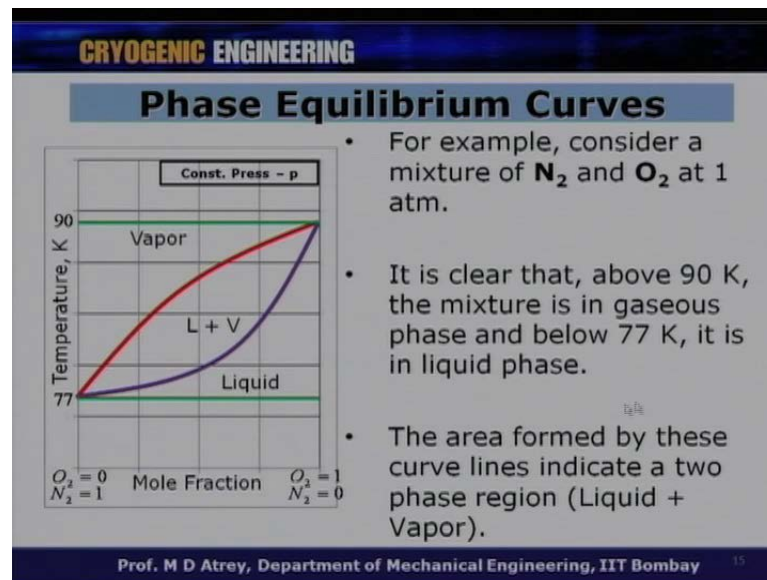
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So, consider a 2 component system which is A and B at some pressure p for which this diagram has been drawn and temperature T . The critical pressure P_c of both these components are more than the pressure P , when you got such a diagram and we will go in the details of this diagram later. What I want to say is when this diagram goes from A is equal to 0 to A is equal to 1 it means that, the critical pressures of both the components are more than pressure basically.

So, basically in this case the P_c of these components are more than the pressure for which this diagram has been drawn. It means that, both the gases now, are below the critical pressure, both the pressure at for which this diagram has been drawn, at this pressure both the gases have this pressure is less than the critical pressures for both the gases basically.

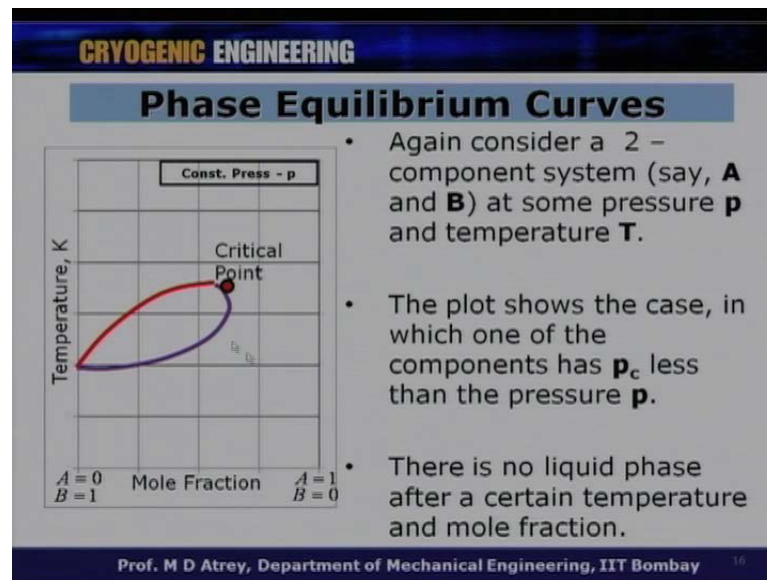
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The plot shows the variation of mole fraction of the components with temperature, this is 1 of the types of the diagram. For example, consider a mixture of nitrogen and oxygen at 1 atmosphere. So this is a case become oxygen is equal to 0, oxygen is equal to 1, oxygen is equal to 1 will have it is boiling as 90 Kelvin at this and nitrogen is equal to 1 will have 77 Kelvin at his boiling, because mixture is at 1 atmosphere. It is clear that above 90 Kelvin the mixture is in gaseous phase and below 77 Kelvin it is going to be liquid phase.

So, this is 90 Kelvin, this is 77 Kelvin below 77 Kelvin the mixture is going to be completely liquid phase above the 90 Kelvin is going to be gaseous phase. The area form by these two curves indicated two phase region. So, this area is going to be a two phase curve here, which is going to be liquid plus vapor. So, below is liquid, top is Gas And what you have is a vapor liquid and liquid plus vapor in this case.

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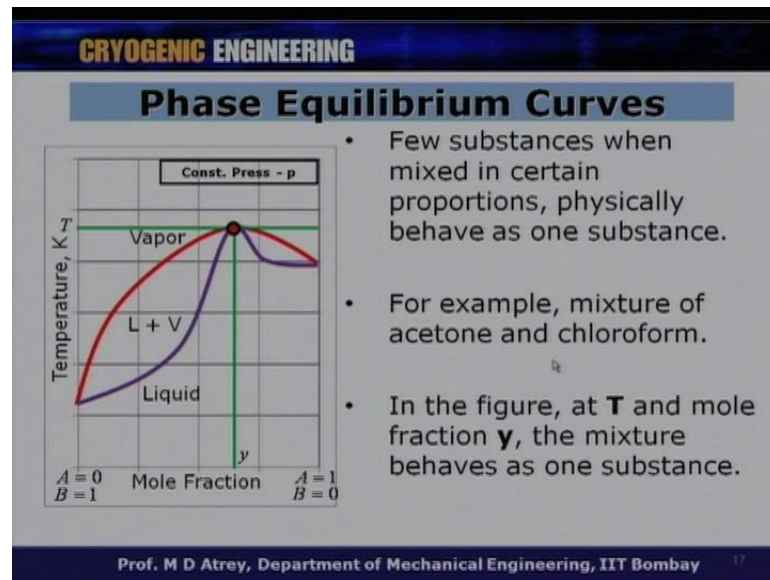
Now, in this case this is a second time of a diagram which is a phase equilibrium curve you have got a 2 component system again A and B at some pressure P and Temperature T. But you see this diagram is not going from this end to that end; that means, the critical pressure is playing a role here. The plot shows in which one of the components has the critical pressure which is less than the pressure p. So, this diagram has been drawn for a some pressure P, but one of the components here as a critical pressure less than this P value and that is why, what you see here is only Gas, what you see here not 2 phase. This was not true in the earlier case, in the earlier case the critical pressure was more than this p for both the gases.

But here, the critical pressure for one of the gases is less than pressure for which this diagram has been drawn. And therefore, above a particular mole fraction of let us say a is what you see is not this region at all; there only Gas in this case. And this is a very typical case normally we will not come across such a case unless we want to draw specific for some cases.

There is no liquid phase after a certain temperature and mole fraction and that is what you can see. After particular temperature and mole fraction there is no liquid phase and this is a very typical diagram of a 2 component mixture. So, you can see beyond this value there is no, beyond this mole fraction there is no liquid. This is one more typical diagram which will hardly will come across, but I just want to complete for the sake of

giving you all the three types of this phase equilibrium curves, what you see here is a typical behavior on this side. So, at this point you can see that, both the vapor and liquid actually at one point; that means, you cannot possible differentiate between vapor and liquid at this point.

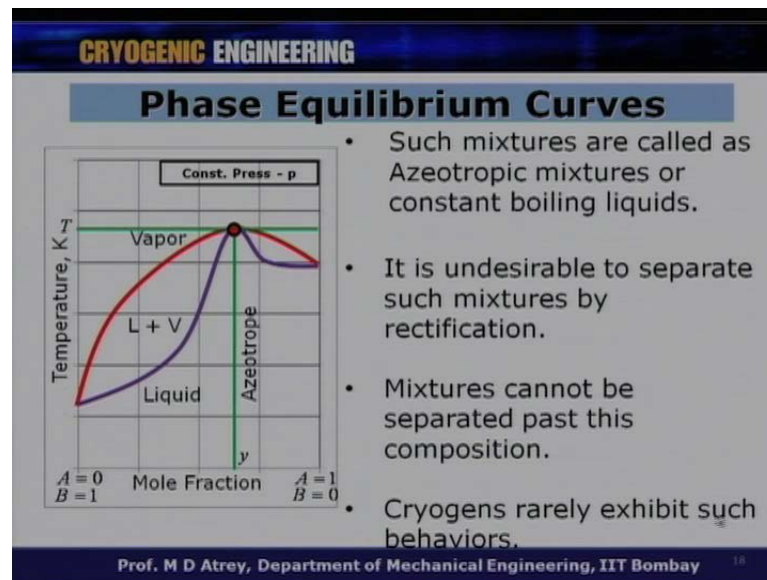
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So, few substance when mixed in certain proportions. So, this happens typically at one molar fractions when A is equal to this much and B is equal to so much, at this particular molar fraction only, you find that both phases are coming together. When mixed in certain proportions physically behave as one substance, they are actually behaving like a 16 (()) you cannot differentiate between this two vapor phases or liquid phases this is at this particular molar fraction; that means, there actually showing a single component behavior over here. And therefore, they behave as one substance in this case.

For example mixture of acetone and chloroform, at a particular proportion a mixture of acetone and chloroform will show such kind of behavior, in the figure at T and fraction of y.

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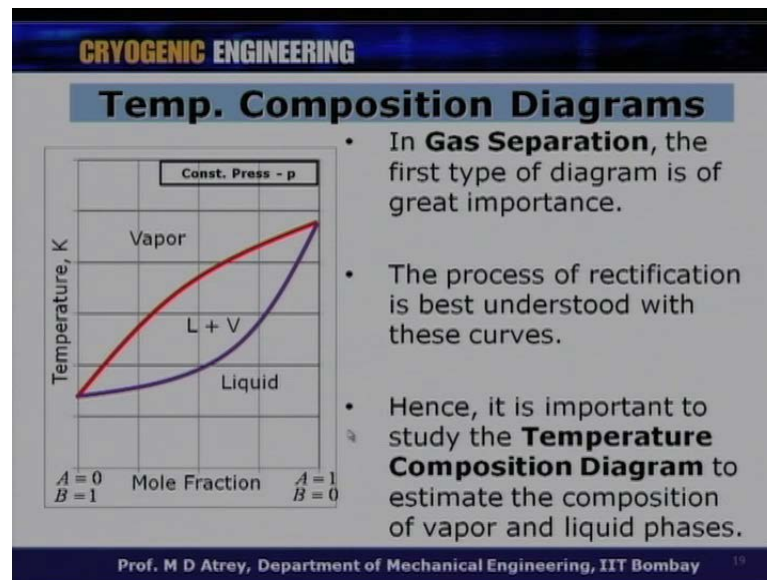


So, at a particular temperature T and particular fraction y the mixture behaves as one substance such mixtures are called as Azeotropic mixtures or constant boiling liquids. What are Azeotropic mixtures? The liquid is constantly boiling, you know you cannot differentiate between vapor and liquid that is why it is called as constant boiling liquids over here. It is undesirable to separate such mixtures by rectifications.

Now, normally such mixtures cannot be separated by what we call as a distillation or rectification, because vapor and liquid cannot be differentiated, they are being Azeotropic in nature. The mixtures cannot be separated past this composition once, we heat this composition, you see on the left side of this your vapor and liquid can be differentiated and therefore, this mixture can be separated. So, below a particular mole fraction if you got a mixture then one can separate, because the vapor region and the liquid region, we can see that you got a vapor and liquid separated out over here. But on the right side of this molar fraction, the material behaviors assist this only one component and therefore, it cannot be separated on the right side of it. Cryogenics rarely exhibit such mixtures.

So, this is; this we will not come across this situation in cryogenics and therefore, they will not be taken. So, having understood the importance of temperature composition diagram for a mixture, let us see the temperature composition diagram for a binary mixture.

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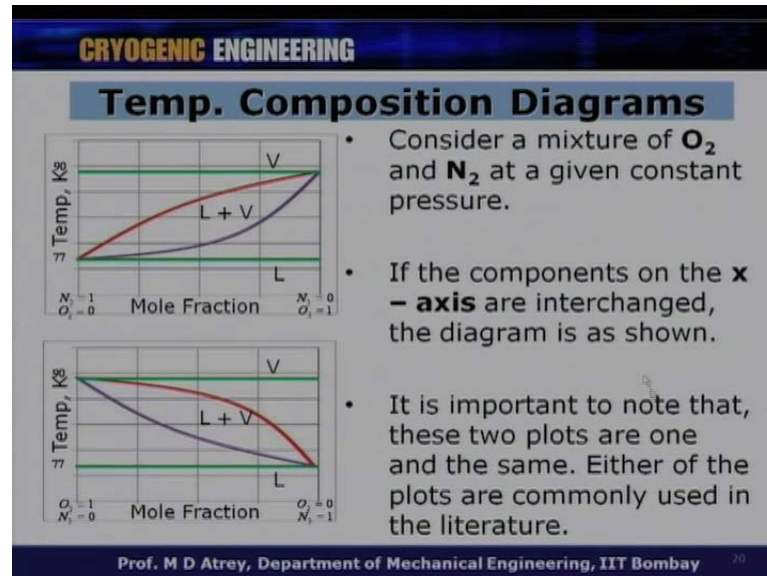
That means, 2 component mixture in Gas separation, the first type of diagram which is what we I just showed you 3 types of diagrams, the first type of diagram is of great importance and this is this diagram. So, from here, you can see that we got temperature on the y axis and the mole fractions on the x axis, this diagram is a very characteristic diagram of A and B components for a given mixture. This is a constant pressure P temperature and molar fractions are the 3 degrees of freedom required for a 2 component mixture for 2 phases.

So, here is a diagram which gives you all the details and now, we will understand this diagram and we will be using this diagram hence forth for all the understanding later. So, let us come to the process of rectification is best understood with these curves and therefore, as I said we will stick to this diagrams now. Hence, it is important to study the temperature composition diagrams to estimate the composition of vapor and liquid phases.

So, basically from here from this diagram, I can get the relationship between temperature and composition of A and B or a mixture. And then, I can understand what is the state of that particular mixture how much vapor? How much liquid? How much molar fraction of A and how much molar fraction of B will be there and this is very important when I go for Gas separation technique or rectification technique. So, this is a typical diagram we just talked about, it can be put for a let us say nitrogen and oxygen, I got a nitrogen is

equal to 1 from this point and nitrogen is equal to 0 over here, oxygen is equal to 0 at point, oxygen is equal to 1 at this point.

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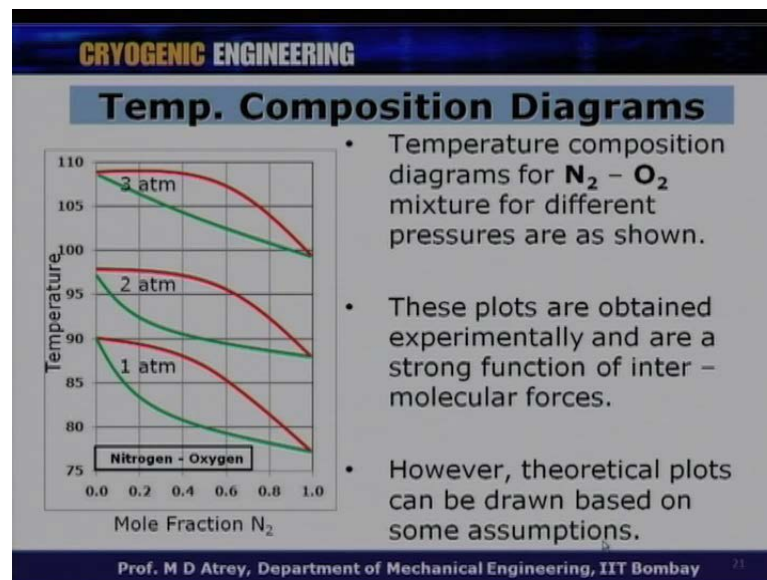
So, consider a mixture of oxygen and nitrogen at a given constant pressure and this is a typical diagram. Now, this diagram can be put in this form and here what you get is oxygen is equal to 1 and therefore, this is nothing but a boiling of oxygen at 1 atmosphere which is 90 Kelvin. And this is the boiling of nitrogen at 1 atmosphere which is 77 Kelvin in between lies both the components. Here O_2 is equal to 0 and N_2 is equal to 1; that means single component at this point, there is a single component at this point, which is oxygen. And therefore, what they have is a boiling of oxygen and nitrogen only.

Now, this diagram can also be put in this way also, in some certain books in reference books, you can have instead of having oxygen is equal to 0, you can have oxygen is equal to 1. That means, the higher boiling component and the lower boiling component could be on any side. So, once you see this point, this is a higher boiling component, because the boiling point of this is higher than the boiling of this. So, by looking at this diagram one should be able to; immediately understand that, in this case the higher boiling component is on the right side and therefore, oxygen is equal to 1 in this case. While here, the left side of the diagram shows higher boiling point, because this temperature is more than this temperature. And therefore, one knows that here oxygen is equal to 1 in this case.

So, you may come across different diagrams from different reference books in order to get varied about this is only that is a O_2 is equal to 1 and N_2 is equal to 0. That means, low boiling component is O_2 in this case, while low boiling component N_2 was equal to 100 percent or 1 in this case. So, if the components on the x axis are interchanged the diagram would look like this, everything remains the same, the whole theory remain the same what is different is only the axis are changed.

So, here what we have 90 Kelvin at this point and 77 Kelvin at this point instead of having it at this point in this case. It is important to note these two plots are one and the same as I said. Either of these plots are commonly used in the literature. So, as I said you can find both the types given in different reference books.

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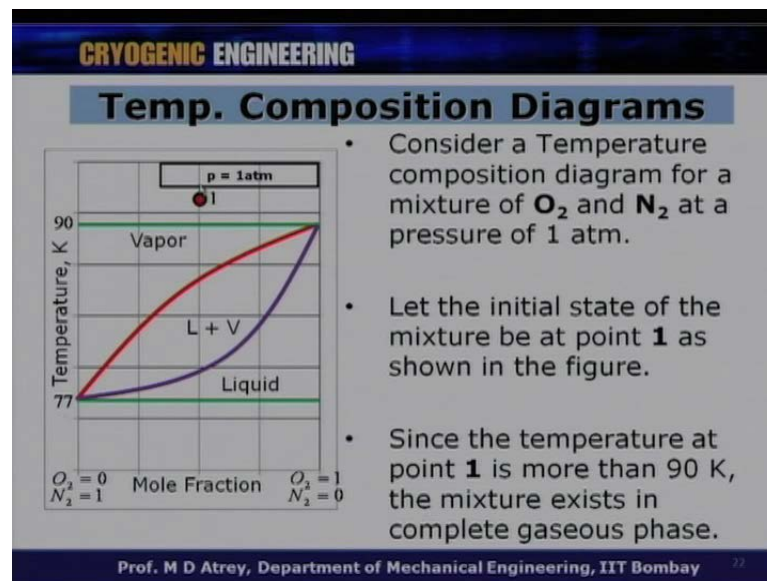


Now similarly, these diagrams could be at different pressures. So, moment as say 1 atmosphere I know 90 77 Kelvin are the respective boiling points. Moment I know the 2 atmosphere I got 97 and something like 87 or 88 Kelvin as the boiling point of nitrogen at 2 atmosphere. Similarly, at 3 atmosphere I got a boiling point of oxygen and boiling point of nitrogen.

So, temperature composition diagram for nitrogen oxygen mixtures are shown at different pressures. These plots are obtained experimentally, this values these are very important plots and we will need this plots, normally there obtained experimentally and they are a very strong function of inter molecular forces. So, experimental values will

take care of all this thing one can compute; however, theoretically also, the theoretical plots can be drawn, but based on some assumptions. So, one will be able to draw this diagrams on a theoretical basis on ideal basis also. And these are the very important diagrams as I said temperature composition diagram, temperature concentration diagram whatever they are called as for a different pressures. Now, look at this typical diagram which will come across all the time.

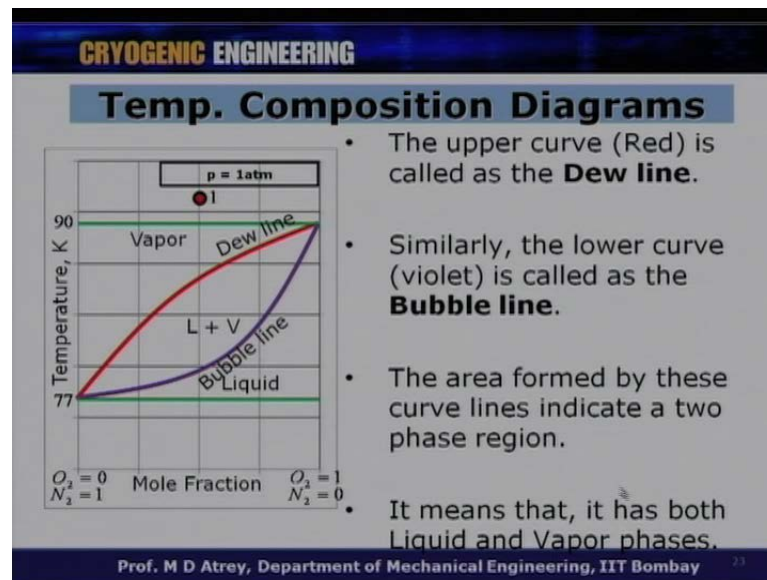
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So, consider a temperature composition diagram for a mixture of oxygen and nitrogen at a pressure of 1 atmosphere. When I say 1 atmosphere the boiling points are fix 77 Kelvin 90 Kelvin, 77 Kelvin nitrogen is equal to 1, 90 Kelvin oxygen is equal to 1 so this is what I just said. Let the initial stage of the mixture be at point 1, I want to show you what happens when the mixture any mixture of oxygen nitrogen is cooled from a very higher point and it comes through this term.

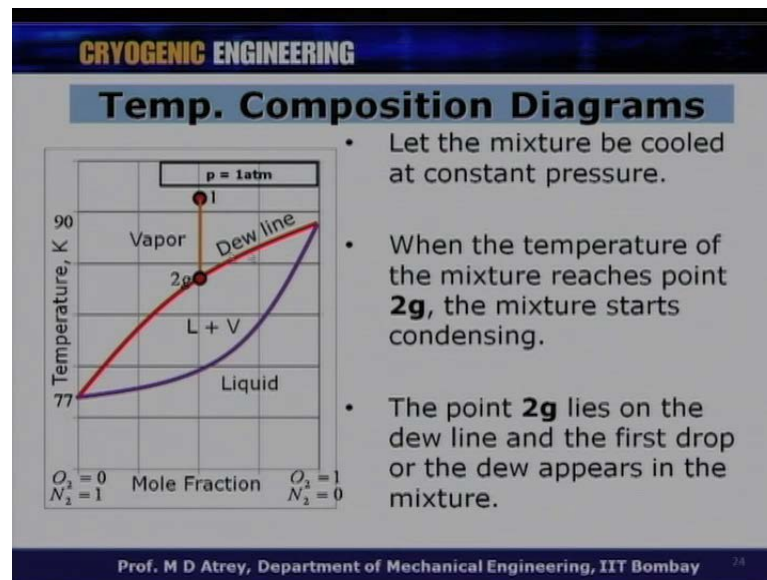
So, what happens to different phases basically? So, let us look at point at 0.1 which is in gaseous phase. Is a mixture at the molar composition at of this mixture is going to be this point let us say 0.5 0.5. So, oxygen is increasing in this direction when nitrogen is decreasing in this direction. So, at this point oxygen is 50 percent nitrogen is 50 percent, the molar fraction of oxygen is 0.5, the molar fraction of nitrogen is 0.5. Since, the temperature at 0.1 is above 90 Kelvin that mean, higher boiling component also the mixture exist in completely gaseous state. So, at this the phase is equal to 1 actually.

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The upper curve is called now, this is a curve which we are going to talk about which is a red curve and you got a violet curve. So, red is called DEW line and this bottom one is called as bubble line and why do we call these lines will understand this. So, there is a basically Dew point or Dew line and bubbles lines. The area form by these two curves indicated by indicated 2 phase region as I written here, you got a vapor over here, you got a l plus v over here. And therefore, it is a 2 phase region this 2 lines and enclose region, actually indicate the liquid plus vapor region and below these what you have is a liquid region. It means that it has both liquid and vapor phases this is what I just talked about.

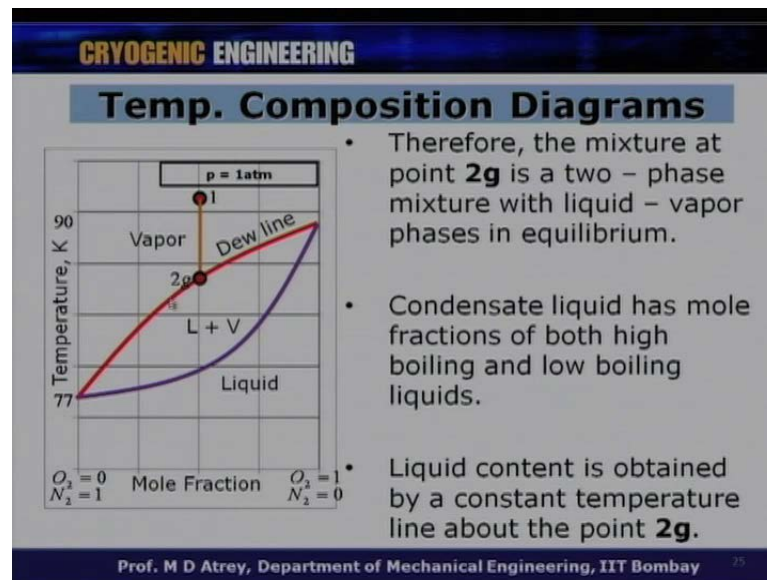
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Now, let us see what happens to this point. Let the mixture which is at 90 plus temperature at this point in time is being cooled at constant pressure and therefore, I am pulling it down keeping the same molar concentration. So, I am coming now, I am cooling it from 90 plus temperature to somewhere here, which is at this point and it this DEW line as I said. What is happening at this point? Suddenly, this single phase mixture gets covered into 2 phase region. So, you got a L plus V now and therefore, the first Dew will appear and that is why this is called as Dew line. When the mixture is cooled it get condensed at this point or some liquid at some vapor or a 2 phase region would appear over here and that is why this is called as Dew line.

When the temperature of the mixture reaches to point 2 g which is this mixture starts condensing. So, the point 2 g now, lies on the DEW line and the first drop of the due appears in the mixture, this what I just said therefore, this is called as Dew line.

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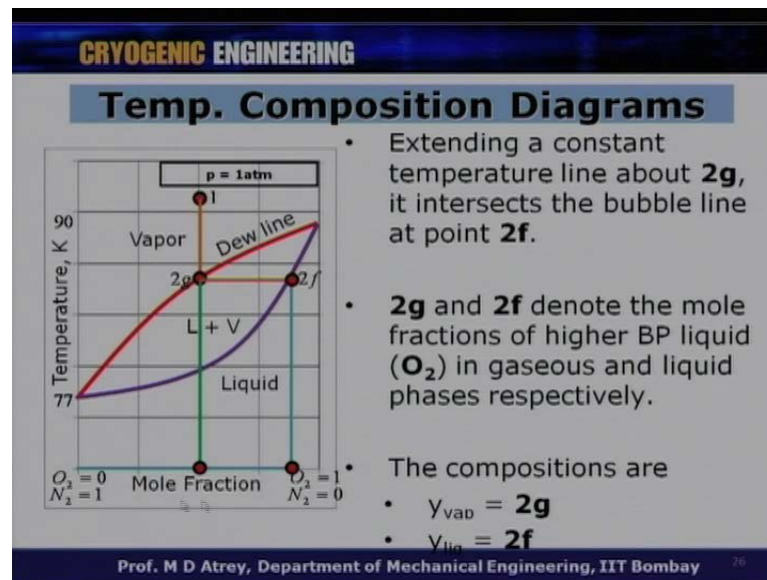


Therefore, the mixture at point 2 g is a two phase mixture with liquid vapor in equilibrium. The moment you decrease the temperature from 1 to 2 g, what you have is a 2 phase mixture, at 2 phase now, you have got a liquid and vapor both of them are in equilibrium both this phases are in equilibrium.

So, I say the mixture is having a molar concentration which is same as this which is at point 2 g, but it has got vapor phase and liquid phase. What are the concentrations of oxygen and nitrogen in vapor and liquid that is what we want to understand now. The condensate liquid has mole fractions of both high boiling component and low boiling liquids. So, we can say high boiling and low boiling some time they are (()) high boiling component, low boiling components high volatile and low volatile will talked about little later also. The liquid content, how do I get liquid, this is a dew line which normally is a kind of a saturated vapor line and this is a liquid line and below this what you have got a liquid line.

As I said the vapor and the liquid are in thermal equilibrium; that means, the temperatures of both the phases is same. So, temperature remaining same; that means, I will like to draw a horizontal line and this horizontal line will heat Dew line at one point and will do will heat the bubble line at 1 point. And therefore, this 2 point will give me the vapor and liquid points respectively.

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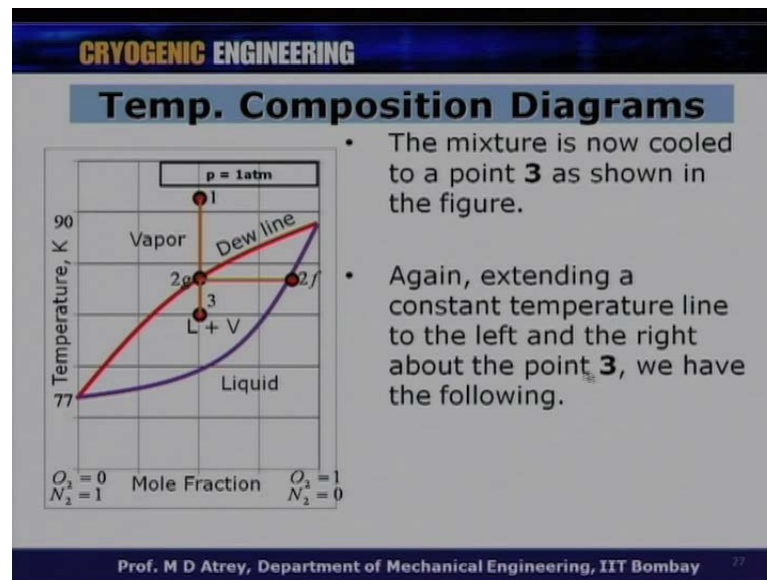


Extending a constant temperature line about point 2 g, it intersect the bubble line at point 2 f. That means, because there is just said the vapor and the liquid line, they will be in thermal equilibrium therefore, it will heat this point at 2 g and will take that 2 f respectively, this is intersecting the bubble line at point 2 f.

So, 2 g and 2 f denote the mole fractions of high boiling liquid in gaseous and liquid phase's, high boiling component in gaseous and liquid phases respectively. So, you have got a point 2 g which has got oxygen is equal to 0.5, which is a high boiling component, while you have got a point 2 f which has got oxygen in very high proportion 0.8 or 0.9 proportion. So, this is liquid and this is basically the vapor point. The compositions are Y vapor I will refer to this as a Y vapor. So, in a vapor region the Y vapor will have a 2 g concentration.

So, around 0.5 is a oxygen vapor and 0.5 is a nitrogen vapor. But in liquid which is at 2 f I got a y liquid at 2 f; that means, almost 80 percent of this liquid will be having oxygen, very 20 percent will be nitrogen. And this is very important that this liquid will have more of high boiling component at this particular temperature, while the molar fraction in a vapor will have 0.5 and 0.5 each.

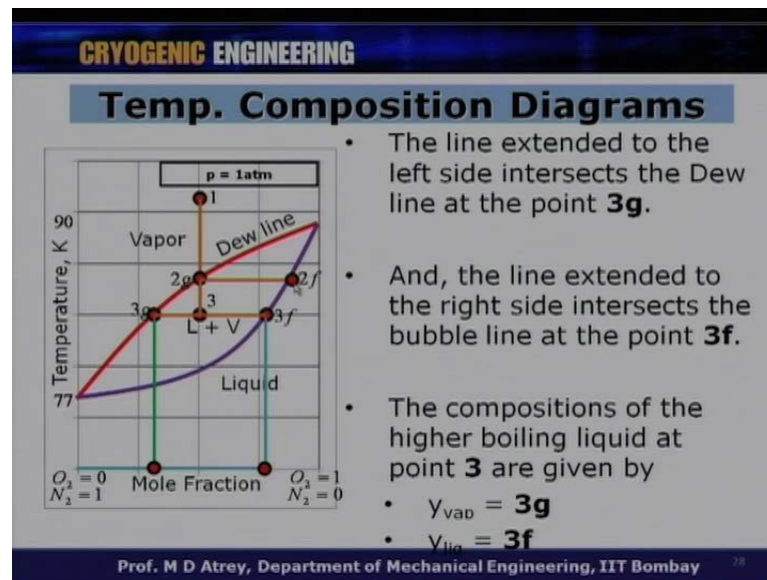
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This we have just cooled will up to 2 g now. The mixture is now cooled 2 a 0.3. So, if I come down further I will come to a 0.3 I shown in this figure. And therefore, I am cooling this liquid now, cooling this mixture from 2 g 2.3; that means, it has come straight in the heart of this 2 phase diagram, are you understanding. Now, basically I was at some point over here and now, I have come down to something like to 85 Kelvin or something like that or 83 84 Kelvin like that, where I am in the heart of this L plus V region.

So, if I now want to see what are my molar fractions of A and B or oxygen and nitrogen in vapor or in liquid fractions? So, I want to see the molar composition of vapor and molar composition of liquid, what will I do in that case I will again draw a horizontal line. Because the vapor and liquid are going to be in thermal equilibrium with each other, the horizontal line where it heats the Dew or Dew line I will get a vapor composition at this and the line which touches the bubble line at one point I will get a liquid composition at that point.

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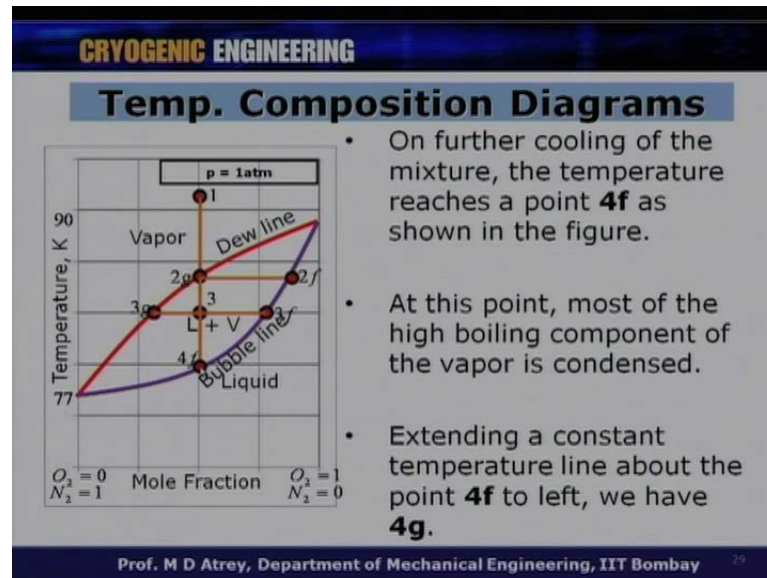
So, again extending a constant temperature line to the left and the right of this 0.3, we have the following, the line extended to the left side intersects 3 g. So, from 3 to I go to 3 g when I am extending this line on the left side and where it intersects the Dew line. Similarly, if I extend this line to the right side it intersects the bubble line at 0.3 f and the line extended to the right side intersects the bubble line at 0.3 f.

So, I have got now two more points which are 3 g and 3 f and 3 g basically will give me the molar fraction of the vapor in which oxygen will be so much percentage and nitrogen will be so much percentage. While the 3 f will give me, the molar composition of the liquid how much oxygen is there? How much nitrogen is there in the liquid which is in thermal equilibrium with this 3 g. The compositions of the high boiling component at 0.3 are given as at 0.3 g are given as $y_{\text{vapor}} = 3g$. So, oxygen now, which is the high boiling component has got less number of mole fraction as compared to the previous points, at the previous it was 0.5 0.5. But as the mixture is cooled further down, the high boiling component oxygen has become less in this, while the y_{liquid} , this is the liquid point, you see the oxygen percentage in this case also has decreased as compared to what it was at 2 f and this is a straight result of cooling of this mixture from 2 g to 3 point.

So, in short what is happening is when you cooled from 2 g to 3 in a vapor region the high boiling component decreased. Also in the liquid region high boiling component decreased it means that the low boiling component increases both in vapor and liquid region. And

this is what we want to do when we are cooling a mixture from a high temperature to low temperature. That means, as you go down cooling this mixture, the percentage of low boiling component will start increasing both in vapor region and liquid region.

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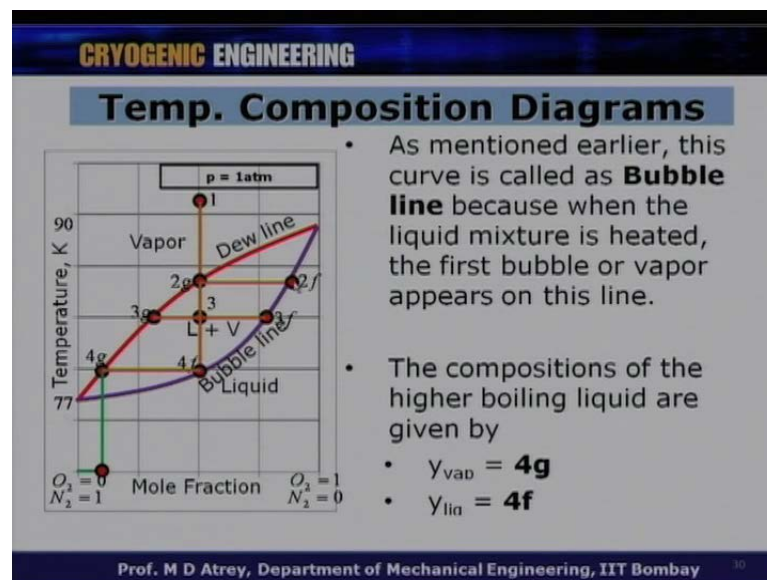
So, let us see what happens if you cool this mixture further down. On further cooling of the mixture, the temperature reaches a 0.4 f. So, if I am now going to first cool down 1 to 2 g, from 2 g I have got 2 g and 2 f then I cooled it further from 2 g to 3 point, where I got 3 g and 3 f in which we just saw that, the high boiling component at vapor and in liquid both decreased. It means that the low boiling component is the mixture in the liquid and both in the liquid and the vapor from increases. Now, if I cool it further down to 4 f at this point it will heat my bubble line. So, now I have cooled the mixture from DEW line to bubble line. So, I have pass through complete 2 phase region and now, I have below these bubble line what we have only liquid.

So, if I want to see now, what is the composition of this mixture when I am reaching this temperature which is going to be it is around 80 Kelvin, at 77 Kelvin what you have is a nitrogen boiling point. So, for any mixture which is between 77 and 90 Kelvin I got a bubble line at this point, let us see what are the composition of this mixture. So, at this point, most of the high boiling component of the vapor is condensed. As you are coming down the high boiling component is getting condensed and also low boiling component is showing up now basically. So, as you cool down the temperature, the high boiling

component get condensed first and that is what we see here at point 2 f and as you come down further the low boiling component also start showing up, because the low boiling now, start getting condensed slowly and steadily.

So, extending a constant temperature line. So, if I want to see now, what is the molar composition of the vapor at this point and what is the molar component of liquid at this point? The liquid is going to be given by the same point which is 4 f, while if I draw a horizontal line I will get a 4 g which will give me the vapor composition. So, if I draw horizontal line which the constant temperature line I will heat 4 g. So, this is my point 4 g.

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As mentioned earlier, this curve is called bubble line, because when the liquid mixture is heated the first bubble or vapor appears. So, here we have come from Dew line and we understood that when this Gas mixture is cooled the first Dew or condensate would appear at this and therefore, it is called as Dew line. Similarly, if I may this point, and if I increase the temperature of this liquid slowly at this point, this is going to the first point that the bubble or vapor will appear and therefore, this line is called as bubble line. So, the bubble line will show up for the first time bubble, when we start heating this liquid, while the Dew line will show when we start lowering the temperature of a mixture. And when it heats this particular temperature, the first dew will appear or the first liquid or

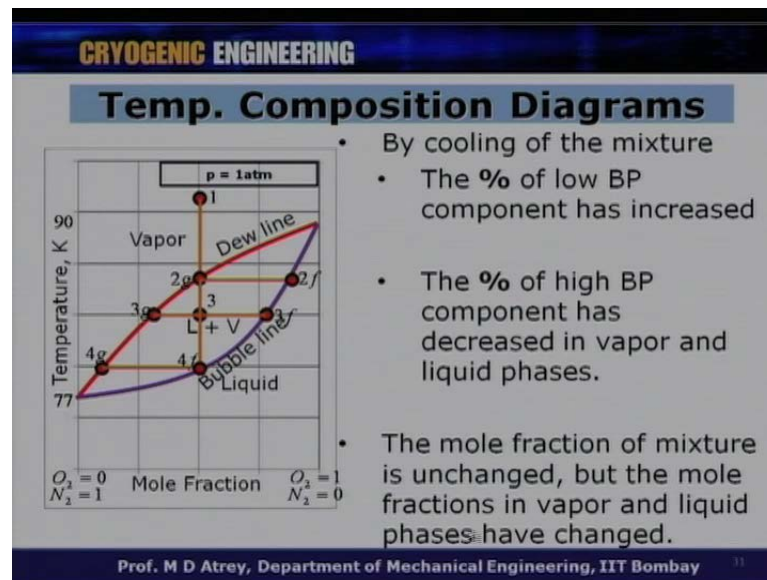
the condensate would appear and therefore, it is called as Dew line I hope you have understood this.

The composition of high boiling components not its come back to this 4 f and 4 g. And now, if I am coming at point 4 g what is going to be the composition? The composition at this point is the vapor composition it going to be 4 g; that means, you can see now the high boiling component is only this much, when we are cooling from here to here. And we are coming close to the low boiling component boiling temperature; the vapor also has got very less quantity of oxygen. That means, the high boiling component as actually becoming less and less, while the percentage of vapor it of nitrogen is much more.

So, oxygen is only going to be around 10 percent, while 90 percent is going to be nitrogen vapor. And similarly, at for liquid what we have is a 4 f, if I take a liquid at this point, this is a liquid line it is 0.5 0.5. So, 50 percent oxygen and 50 percent nitrogen when in the first case 2 f it was let us say 90 and 10, 90 percent oxygen and 10 percent nitrogen, at point 3 f, we have around 80 percent oxygen and 20 percent nitrogen. But here at 4 f what you have is 50 percent nitrogen and 50 percent oxygen which means that, as you go on lowering the temperature of the mixture, the low boiling components in a vapor and liquid form have increased. But if you at this the high boiling components are more when you are at a Dew it basically depends on molar fraction start with, because we started at 0.1 instead of this if I started at 0.1 b here, then I would have come very close to this point, because my high boiling component where very less in this case.

So, it all depends on what is your molar composition of mixture and at what point you enter this come down. If I start from the right side at this point; that means, my high boiling components or oxygen percentage is going to be very high initially only. So, initial molar composition is what will decide, what is going to be your relative molar composition at different vapor and liquid lines. This is a very important thing to understand one should be very clear about this DEW line and bubble line the vapor compositions and the liquid composition. So, the respective 4 g and 4 f points which will give you vapor composition and the liquid composition of the mixture at this point.

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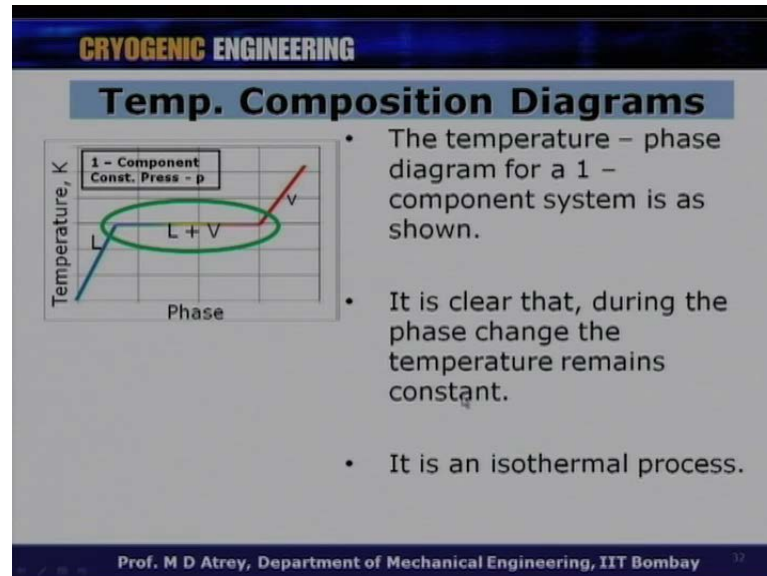
So, what do we understand by cooling the mixture which is what I have been saying all through. By cooling the mixture the percentage of low boiling component has increased. So, if when I am cooling it from 1 to 2 g, 2 g to 3 and 3 to 4 f what is happening is the percentage of low boiling component has increased while the percentage of high boiling component is decreasing slowly. The percentage of high boiling component has decreased in vapor and liquid phases, if you see this vapor the percentage of high boiling component oxygen has decreased. If you see this liquid the percentage of oxygen which is high boiling component has decreased.

What is happening to mixture? The mixture molar composition is remaining the same, if I am coming down vertically and my initial molar composition of mixture is 1 that is going to be remaining same I am not going to do anything with 0.5 0.5. But if I say respective vapor and liquid composition that is going to be different, the liquid actually will remain the same basically, because we are going to be touching the same molar composition.

So, we can say that the molar composition of mixture at all the points is going to be remaining same, because we are travelling vertical down. But the vapor and the liquid will have different molar compositions of respective high boiling component and low boiling component. This is what I want to say at the end, the mole fractions of mixture is

unchanged. But the mole fractions of vapor and inlay vapor and liquid phases have change and this is what we understand from cooling of this mixture.

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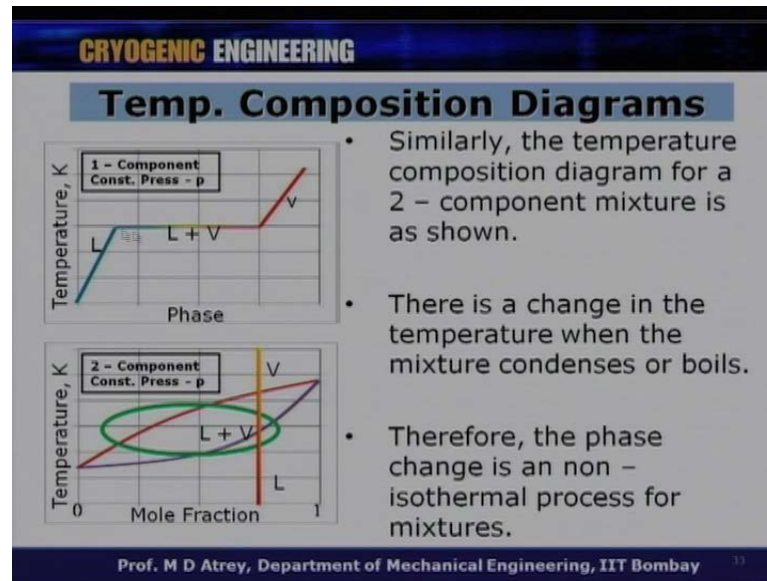


So, having understood this temperature composition diagram and having understood the what happens to the molar composition when we start cooling this mixture. Let us see what we have understood from this, the temperature phase diagram for a 1 component system is normally like this. So, if I start cooling 1 component I am coming down from this vapor region and during this phase transition I got a 2 phase region. And therefore, I got a L plus V over here and as you know for a single component during the phase transition the temperature remain constant.

So, when I got an L plus V shown over here, is it a completely horizontal line if a plot temperature versus phase. So, here the vapor composition is coming down this is a L plus V and then what you see is L further down and then it will become solidification. So, what is important to understand is for a given pressure, during this phase transition vapor to liquid you got an L plus V region which is a 2 phase region and during this transition temperature remains constant. So, it is clear, that during phase change the temperature remains constant and this is a very known factor, when ice becomes water or when water becomes vapor during this phase transition, you got a temperature remaining constant as 0 degree centigrade and at 100 degree centigrade and is a known fact.

Now, let us see what happens in a not a single component, but what we have got a mixture of 2 components and let us see what happens to that and what happens to the temperature during the phase transition. So, in a single component what we say is a phase change is an isothermal process is an isothermal process, because the temperature remains constant.

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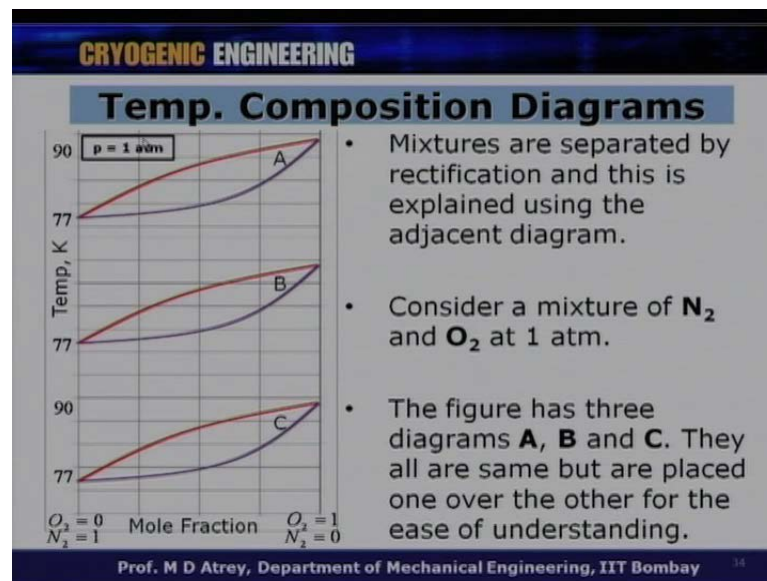
Now, this is a diagram which is what we have just seen where we plot temperatures for a given mole fraction and if I go on reducing the temperature how you see the phase now. Similarly, the temperature composition diagram for a 2 component mixture is as shown, what you see here is this vapor will touch Dew line, you get a condensate at this point and then you got a L plus V region. Now, when I am heating this L plus V region my temperature is going down and still I am having phase change which is possible over here and here I meet liquid region.

So, the vapor will get completely converted to liquid, when I am cooling down this vapor pass through L plus V region and then go to liquid, what does that mean? It means that the phase transition is happening in this region. But during this phase transition as you can see over here, the temperature is not remaining constant the temperature is reducing. And this is a major change when we go from a single component system to a 2 component system. There is a change in the temperature when the mixture condenses or boils. So, it is not an isothermal process, the phase change in a 2 component mixture

when it is subjected to cooling or boiling or heating whatever. Whenever there is the phase change that occurs one needs to increase or decrease temperature in order to have complete phase change, phase transformation. In order to go from vapor to liquid you pass through a 2 phase transition, but in order to achieve that completely you have to decrease the temperature all through.

This means that the phase transformation in a 2 component system or at any mixture of 2 or 3 different components is not an isothermal process; the temperature does not remain constant during the phase change. Therefore, the phase change is a non isothermal process for mixture, while it was a isothermal for a single component system and this is a major change when you go from single component to multicomponent mixtures. Having understood this now, let us come to a very important aspect, why are we doing all this things? We are trying to understand a temperature composition diagram so has to understand the mixture separation.

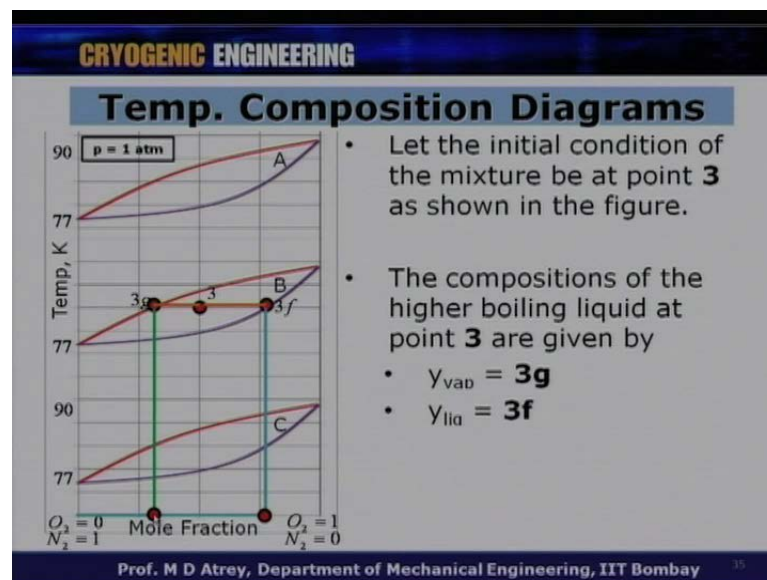
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So, what is this, I just want to give a small glimpse, we will go in the details of this mixture separation further, but I just want to give a some basics as to why I am doing all this things. And this is what these three figures will show you, why are we doing all this thing, how does this help me in separating mixtures oxygen and nitrogen for example, in this case.

So, mixtures are separated by rectification and this is explained using the adjacent diagram. Consider a mixture of nitrogen and oxygen at 1 atmosphere. Let us say, the figure has three diagrams, which is A B and C they are all the same actually, they are all having 77 and 90 Kelvin; that means, they are all drawn at 1 atmosphere only. I am just showing repeat of one diag A B and C are essentially absolutely same diagrams, because I want to show different processes, it may not be possible to show all the process is one diagram and I am showing it in three diagrams they all the same diagrams. But are placed one over the other for ease of understanding alright, do not get confused by A B C basically, essentially they are the same I am just showing some process is in B, some process is in C and some process in A.

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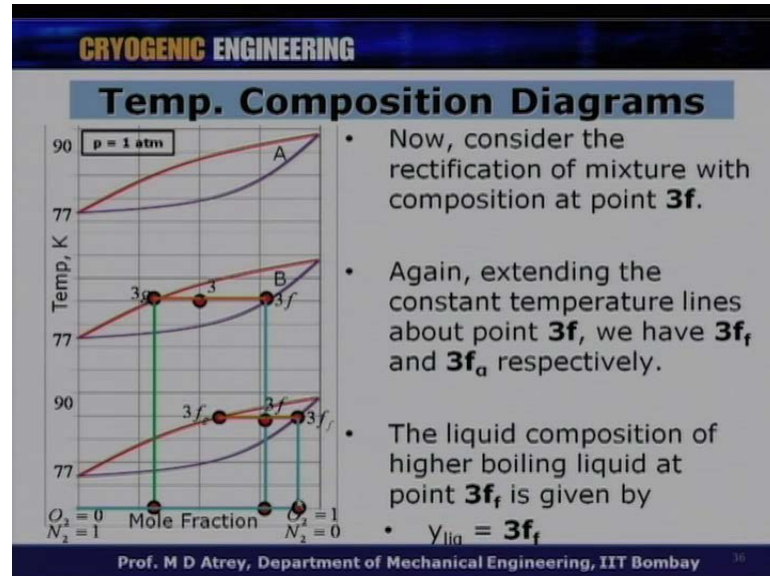


So, let us initial condition of the mixture be at 0.3, let us say the molar fraction of the mixture to be separated have 0.5 0.5 oxygen and nitrogen let us say. So, when I come in this middle diagram I start with B first and I am let us say that 0.3. Now, let us find out corresponding vapor and liquid molar fractions as we have done earlier. If I draw a horizontal at this line, the point where in intersect the bubble line will give me the liquid fraction, the point will where it intersects the Dew line it will give me a vapor fraction.

So, the composition of the higher boiling component at 0.3 is given by 3 f and 3 g. So, y vapor, 3 g gives me vapor condition, 3 f give me liquid conditions, the vapor composition at 3 g oxygen high boiling component oxygen is going to be given by 3 g.

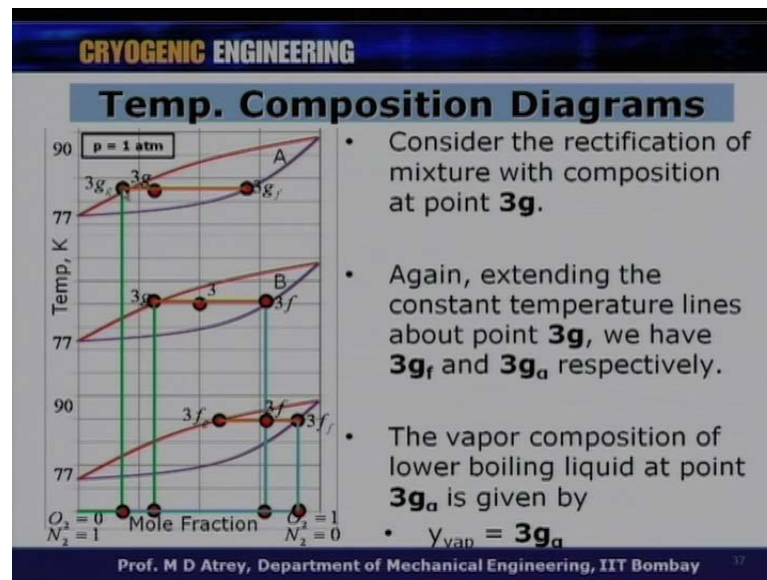
So, this 3 g is basically, nothing but vapor composition or vapor fraction of high boiling component, while the liquid composition of the high boiling component will be 3 f. So, y liquid is 3 f.

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So, when I am have maturing at 0.3, the liquid have higher molar fraction of high boiling component, while the vapor will have 3 g mole fractions of the high boiling component. Now, what I am going to do is, I am taking this liquid from here. So, this is my first process in rectification, I am going to take this liquid and I am going to have this molar fractions of liquid plus Gas entering the same temperature composition curve again. So, I will get some vapor fraction now, added to this. So, I got a 2 phase now, again and this will enter the same, this liquid plus vapor will enter the same vapor temperature composition curve at this now.

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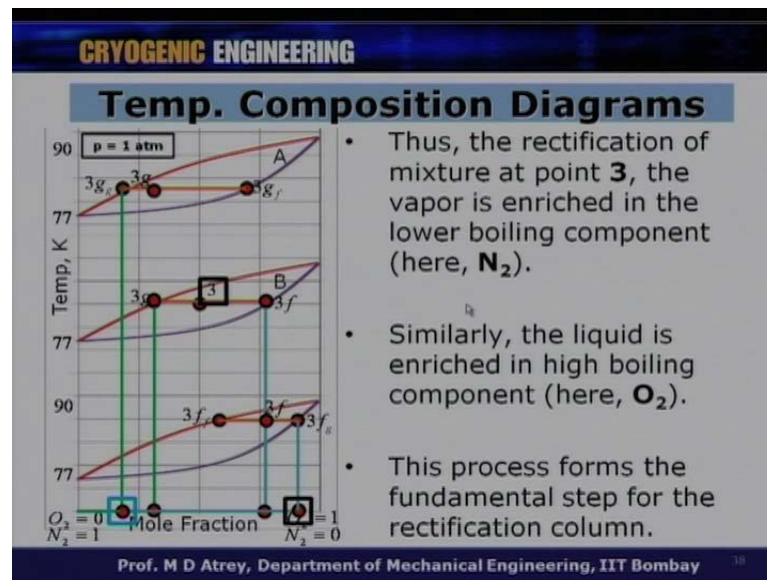
Now, consider the rectification of a mixture with composition at 0.3 f. So, what is going to be by 3 f? I got oxygen so much and nitrogen so much. And now, I will have a 2 phase flow entering the same region at point, which is the composition given by this point. So, what will happen I will bring this point in a 2 phase region, which I have got oxygen and nitrogen give as same composition. What will happen? This point will further have 3 f f as a liquid composition and the corresponding vapor composition will be 3 f g. But now, I am interested only in liquid composition and what you can see now, when the molar composition of the mixture is 3 f when it enters, when it get enters this vapor composition curve, the percentage of high boiling component in the liquid has increased.

And this is what I am doing repetitively now, what I will do now further, I will further have this composition and the liquid plus vapor at this composition will enter this diagram again. So that I am going towards right side and my right most point is nothing but oxygen is equal to 100 percent that is 100 percent high boiling component. The objective of doing this, objective of the repeating this process and entering again the same curve is basically, to reach the right most point which is 100 percent oxygen; that means, my liquid is getting richer and richer in high boiling component. So, again extending the constant temperature lines about 3 f, we have 3 f and 3 f g respectively, the liquid composition of the higher boiling component 3 f will be given as y liquid which is 3 f at this which is richer what it was at this point.

So, what I am going to do is, I will repeat this again and again, so that I will reach to the right most quantity. So, the liquid is going to be condensed again and again at rich light. Now, let us come back to what will I do with the paper again with this composition now, I will enter this region and now, I will use a in order to explain that. So, consider the rectification of mixture with composition at 0.3 g. And now, I will go into this diagram again and let us see I have entered with this composition in a 2 phase region over here. And let us see what is happening to the liquid and Gas Composition extending the constant temperature line about 0.3 g, we have 3 g f which is a liquid part of it and 3 g g which is the Gas part of it or vapor part of it.

The vapor composition of lower boiling component at this 3 g g is given by y vapor 3 g g. So, what is happening is at 3 g now, I got a vapor at this point in which the high boiling component has decreased, the high boiling component is the less than what it was at this, while the lower boiling component has increased. So, what is basically happening is, the liquid which I get at this first I will go on condensing it till I heat the right most point and I will get 100 percent oxygen liquid from my condensate will be 100 percent richer in high boiling component. While my vapor is going to be richer and richer, because if I go on condensing this vapor of this left composition again and again, I will ultimately would reach the 100 percent low boiling component which is nitrogen. And at ultimately my vapor is going to be 100 percent rich in low boiling component, while my liquid is going to be 100 percent rich in high boiling component and this is what basically, principle of rectification is. Thus the rectification of mixture at 0.3 the vapor is enrich in low boiling component.

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Similarly, the liquid is getting rich in high boiling components, we can see that liquid is getting richer in high boiling component and the vapor is getting richer in low boiling component and this is what we call as separation. Ultimately this vapor is going to be condensed at the last point and I will get liquid nitrogen at one point and liquid oxygen at other point.

So, depending on what is my entry point, ultimately what I am going to do is reach to the right most point and reaches to the left most point. So, right most point is 100 percent oxygen left most point is 100 percent nitrogen and this is what I do is basically go on repetitively going on condensing my mixture and reaching to the right most and the left most point and this I what we call as rectification. So, this is what is basic principle of Gas separation at in cryogenic condition. This process forms the fundamental step of the rectification column exactly this is going to be achieved by a device called as rectification column which will see in detail in the coming discussion.

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CRYOGENIC ENGINEERING

Summary

- If number of components, number of phases and degrees of freedom for a mixture in thermal equilibrium are denoted by C , P and F respectively, then the Gibbs Phase Rule
$$F = C - P + 2$$
- The variation of mole fraction (y) with temperature (T) at a constant pressure (p) is given by **Temperature composition diagram** or **Phase – equilibrium curve**.
- Condensation or boiling of a mixture is a non – isothermal process.®

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So, in order to summarize what we have done till now. First we talked about Gibbs phase rule, if number of components number of phases and degrees of freedom for a mixture in thermal equilibrium are denoted by C , P and F respectively. Then Gibbs phase rule give you F is equal to C minus P plus 2 and we have seen several examples for different components and different phases. The variations of mole fractions Y with temperature at a constant pressure P given by temperature composition diagram or a phase equilibrium curve and we understood that how important it is in order to understand that characteristic of any mixture.

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CRYOGENIC ENGINEERING

Summary

- Repeated rectification of a mixture enriches the liquid and vapor phases with high and low boiling components.

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Condensation or boiling of a mixture is a non isothermal process, which is a very important thing, while it is an isothermal process for a single component. Repeated rectification of a mixture enriches the liquid and vapor phase with high and low boiling components. So, the liquid is getting richer in high boiling component, the vapor is getting richer in boiling component and this from a basic principle of rectification. We got a self assessment test at the end, please go through those slides; kindly asses yourself, because that will give us a kind of feedback **feed back** to you as to what you have understood from this lecture. So, just small little cross questions and at the end of this, we got an answers given here. Please go through this self assessment. Thank you very much.