Cryogenic Engineering
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Lecture No. #21
Gas Separation

So, welcome to the 21st lecture on a Cryogenic Engineering, under the NPTEL program. Just to give a brief of what we did in the last lecture, I will just summarize some points, and then we will go to the topic of our Gas Separation.

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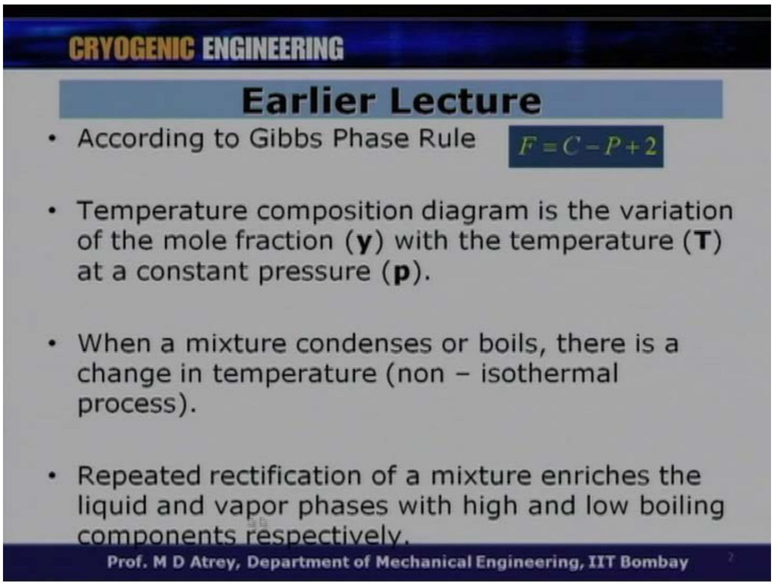

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Earlier Lecture

- According to Gibbs Phase Rule $F = C - P + 2$
- Temperature composition diagram is the variation of the mole fraction (**y**) with the temperature (**T**) at a constant pressure (**p**).
- When a mixture condenses or boils, there is a change in temperature (non – isothermal process).
- Repeated rectification of a mixture enriches the liquid and vapor phases with high and low boiling components respectively.

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Last time we had studied Gibbs Phase Rule, which is basically given as F is equal to C minus P plus 2, where F is degrees of freedom or the intrinsic properties requirement to be specified for any mixture. C is a component, and P is number of phases.

Also we understood about a temperature composition diagram, and it gives the variation of mole fraction that is Y, with temperature T at constant temperature. So, we may talk about any mixture, the number of phases are 2, if we talking about 2 phase mixture or mixture separation by lowering of temperature, we got 2 components.

And therefore, we require some degrees of freedom or the values of F in there, if you got a 2 components, 2 phases or a single phase, we require particular number of properties to be specified. Whenever we talk about mole fraction, what we require is a… whenever talk about a mixture, what we require is a mole fraction Y to be specified of a component A, and component B. And these are very important diagram. These are very important relationships which have to be known in order to specify a mixture. For example, 2 components, 2 phase, we need to have 2 values to be known to us, we need to have 2 degrees of freedom, which could be pressure, and mole fraction or temperature and mole fraction for a given pressure.

When a mixture condenses or boils; that means, when a change of phase happens, there is a change of temperature and this is a non-isothermal process which we saw last time. During condensation of a single component, the temperature remains constant. During the phase the temperature remains constant which is to be the condenses as well as for boiling.

However, for a mixture we have seen during the last last time when I had presented the temperature mole fraction or TY diagram, we have found that during the change of phase, the temperature decreases which means that the process of condensation or boiling is not a isothermal process, is a non-isothermal process, which is a very important deviation from whatever we will learning from normal 1 component system.

We also found that the repeated rectification of a mixture enriches the liquid and vapor phases with high and low boiling components respectively. We had seen that when the mixture is being condensed or vaporized repetitively, what you get ultimately is a high boiling component liquid, liquid at high boiling component and slowly we get on the repeated rectification process, we get a vapor phase, getting richer and richer in the low boiling component.

For example we had seen for Oxygen Nitrogen mixture that when you go on the rectifier in repetitive manner the liquid will get richer in Oxygen or what you get is a liquid Oxygen at 1 end which is 100 percent Oxygen then and the vapor phase will get richer in Nitrogen gas, Nitrogen vapor.

So, ultimately what we do is basically condense this vapor in order to get liquid Nitrogen, but what is important is to understand that the 1 phase, the liquid phase gets richer in a high boiling component which is Oxygen for a Nitrogen Oxygen mixture and the vapor phase get richer in low boiling component which is Nitrogen in this case.

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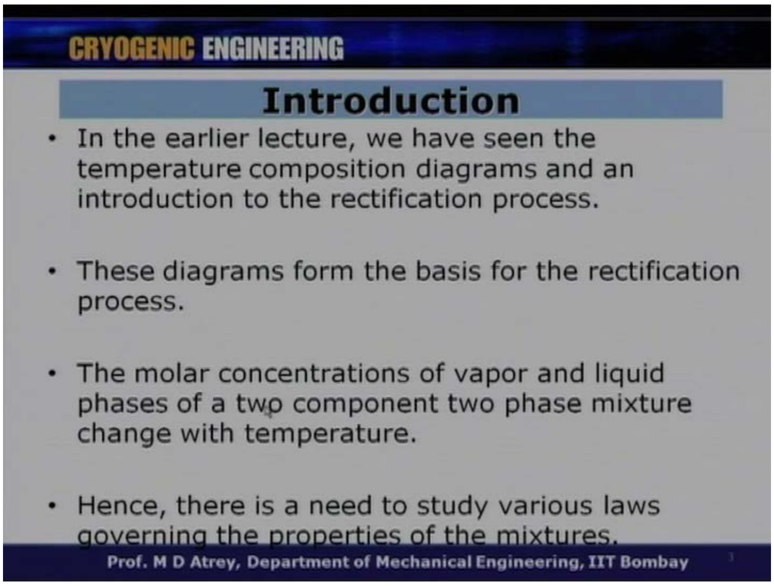

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Introduction

- In the earlier lecture, we have seen the temperature composition diagrams and an introduction to the rectification process.
- These diagrams form the basis for the rectification process.
- The molar concentrations of vapor and liquid phases of a two component two phase mixture change with temperature.
- Hence, there is a need to study various laws governing the properties of the mixtures.

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So, in the earlier lecture we have seen the temperature composition diagram and we also introduced those diagrams how they can be exploited to understand the rectification process which is happens in actually rectification columns. These diagrams form the basis of rectification process.

The molar concentration of vapor and liquid phases of a 2 component 2 phase mixture change with temperature this is what we saw at every point during condensation during the phase change, we saw that vapor phase get richer, richer in low boiling component while the the liquid phase getting richer and richer in high boiling component this is what we just studied in the last slide also.

And this is what exactly happens as the temperature gets reduced the vapor phase will still get richer in the low boiling component and the liquid phase will still get richer in a low boiling high boiling component.

Hence, because this diagrams also critical, because this mixtures have to be ultimately separated from in the rectification column what is important is to understand the basic laws which govern this mixture because this is going to be use every time.

So, hence what we understood is there is a need to study various laws governing the properties of the mixture and therefore, in this particular lecture, what we are going to study is mostly the properties which govern this mixture.

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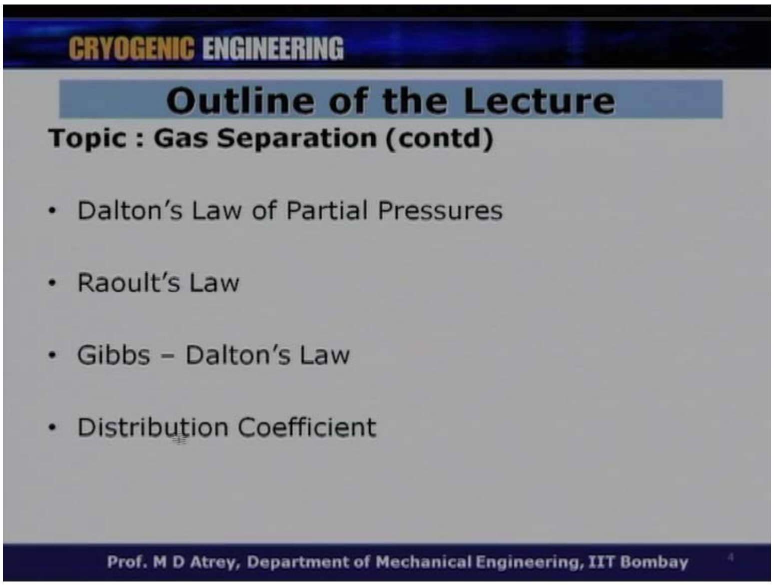
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Outline of the Lecture

Topic : Gas Separation (contd)

- Dalton’s Law of Partial Pressures
- Raoult’s Law
- Gibbs – Dalton’s Law
- Distribution Coefficient

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Outline of this lecture is, we will have to study the Dalton’s law of partial pressure which possibly you must tell studied that. We will have to repeat this again for mixtures now then very important law is the Raoult’s law and then we got a Dalton’s law plus Raoult’s law also. Then we also got a Gibbs Dalton’s law.

And then we come to understand what is the basics significant of a distribution coefficient concept, what is this, how do it play very important role in a rectification column theoretical analysis and finally, all this things could be understood better when we got some tutorials. So, I have got 2 tutorials where we can understand the application of these laws from gas separation point of view.

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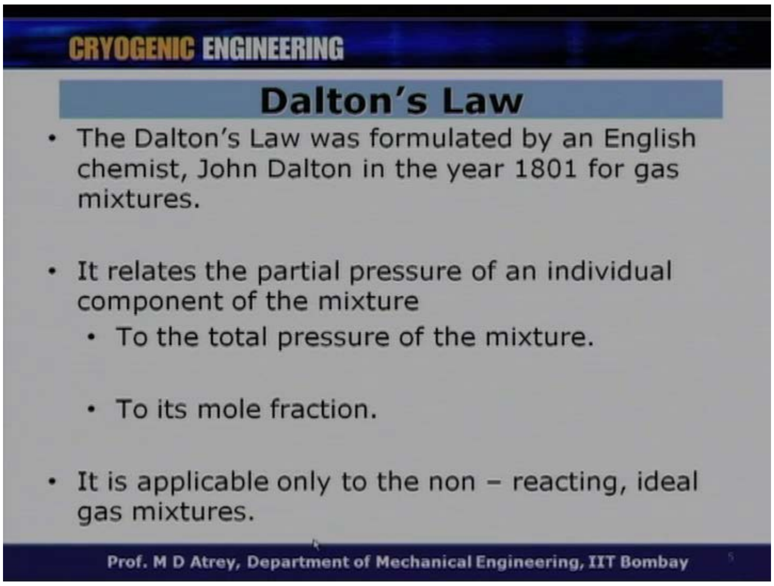

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Dalton's Law

- The Dalton's Law was formulated by an English chemist, John Dalton in the year 1801 for gas mixtures.
- It relates the partial pressure of an individual component of the mixture
  - To the total pressure of the mixture.
  - To its mole fraction.
- It is applicable only to the non – reacting, ideal gas mixtures.

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So, let us come to Dalton's law. The Dalton's law was formulated by an English chemist john Dalton in the year 1801 for gas mixture. So, is a very old law we can see that is almost 200 year old law basically and it has definitely been applied over a product time for gas mixtures.

It relates the partial pressure of an individual component of the mixtures, mixture has got various components and various components will be in the mixture, in different proportion the molar fraction will be different and the partial pressure therefore, will be different of each component in a given mixture. Dalton's law relates basically this partial pressure to the total pressure of the mixture and you'll see now how it does.

So, this relates the partial pressure of an individual component of the mixture to the total pressure of the mixture and to its mole fraction, it is a very simple law, I am sure you must have studied this law earlier, but mathematically I will relate this law to the total pressure of the system.

It is applicable only to the non-reacting ideal gas mixtures. So, this is very important thing that we will not come across non-reacting ideal, our mixtures will be real mixtures. So, this will basically govern the ideal gas mixtures.

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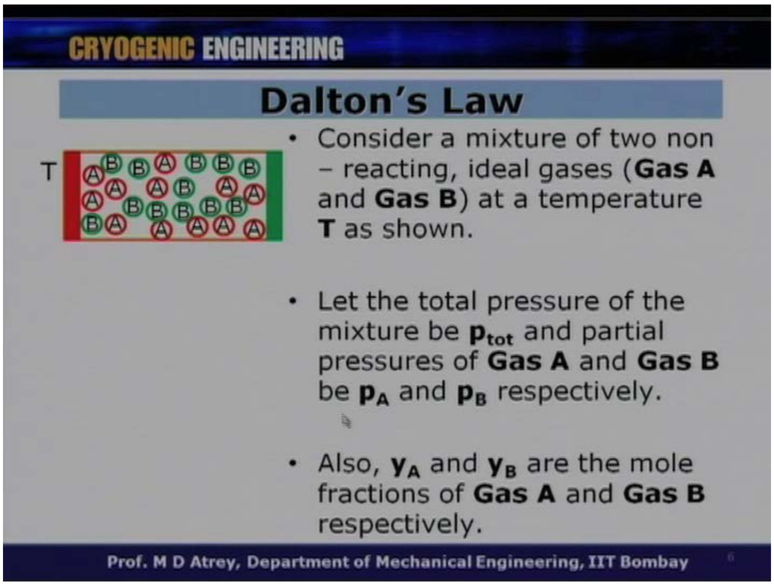

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Dalton's Law

- Consider a mixture of two non – reacting, ideal gases (**Gas A** and **Gas B**) at a temperature **T** as shown.
- Let the total pressure of the mixture be $\mathbf{p_{tot}}$ and partial pressures of **Gas A** and **Gas B** be $\mathbf{p_A}$ and $\mathbf{p_B}$ respectively.
- Also, $\mathbf{y_A}$ and $\mathbf{y_B}$ are the mole fractions of **Gas A** and **Gas B** respectively.

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But we can formulate for real mixtures also. So, simple illustration is consider a mixture of 2 non-reacting ideal gases. So, ideal gases being Gas A and Gas B at a temperature t, so, I have just shown a small cylinder where Gas A has got some component Gas B has some component and in this mixture as you can see in a given enclosure that we have got some component of Gas A and some component of Gas B.

Let a total pressure of the mixture be p total and the partial pressure of Gas A and Gas B be p A and p B because they are present in partiality, you got a in a the pressure total pressure is p total and depending on the presents or amount of Gas A and Gas B it will have its partial pressure which could be p A and p B denoted respectively.

Also the y A and y B are the mole fractions of Gas A and Gas B. So, how much mole fractions if they got a 0.2 mole fraction of y A and 0.8 mole fraction y B or think like that depending on how much quantity of Gas A and Gas B is there in a given enclosure which will decide the molar fraction of y A and y B.

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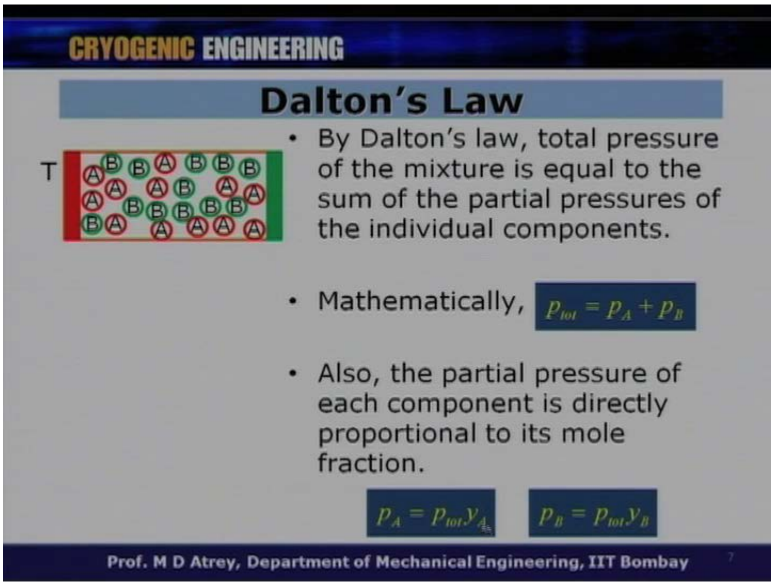

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Dalton's Law

- By Dalton's law, total pressure of the mixture is equal to the sum of the partial pressures of the individual components.
- Mathematically, $p_{tot} = p_A + p_B$
- Also, the partial pressure of each component is directly proportional to its mole fraction.

$p_A = p_{tot} y_A$ $p_B = p_{tot} y_B$

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By Dalton's law, the total pressure of the mixture is equal to the sum of the partial pressure of the individual components. So, it is a very clear and simple law that p total will basically depend on the sum of partial pressure of individual component that is p A and p B.

So, mathematically I can write p total is equal to p A plus p B this is a total pressure of the mixture is equal to the sum of the partial pressures of Gas A and Gas B as you can see from here. Also the partial pressure of each component is directly proportional to its mole fraction.

So, if I want to compute the value of p A, the p A will basically depend on what is the value of y A, p B will depend on what is the value of y B. And mathematically p A is going to be equal to p total into y A and p B is basically equal to p total into y B and this is. So, what we can say is p is directly proportional to y A, p B is directly proportional to y B and the constant of proportionality could be p total in both the cases.

So, once I know what is my mole fraction of y A and y B or a Gas A and Gas B and if I know the total pressure of the mixture, I can compute p A and p B directly. And that is what a Dalton's law of a gas mixture. It will give us conversion of molar fraction to p A and p B for the partial pressures and then what we can compute is a p total.

Extending it to general statement to the mixture of n components we will have following the total pressure p total is equal to sigma p j when j is ranging from 1 to N for N component mixture I think this is very simple and clear.

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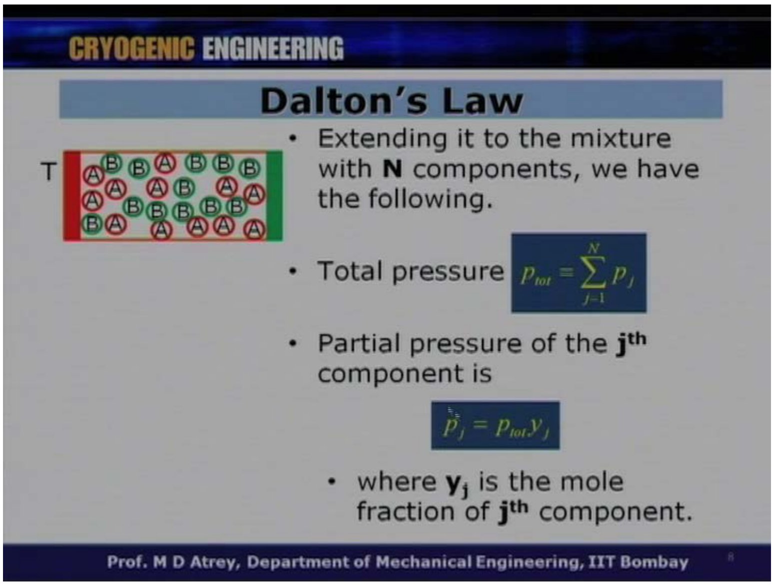

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Dalton's Law

- Extending it to the mixture with **N** components, we have the following.
- Total pressure $p_{tot} = \sum_{j=1}^{N} p_j$
- Partial pressure of the **j**th component is

$$p_j = p_{tot} y_j$$

  - where $\mathbf{y_j}$ is the mole fraction of **j**th component.

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And the partial pressure of the j the component is given by P j is equal to P total into Y j. So, depending on the value of mole fraction of a j the component and depending on the value of p total or the pressure of the total pressure of the mixture, we can compute the partial pressure of j th gas, j th mixture, j th component.

So, where y j is the mole fraction of the j th component. So, one can find out the partial pressure depending on the molar fraction and if we know the partial pressure we can find out the total pressure of the mixture.

Now, extending further from Dalton's law, having understood the basics of Dalton's law, now we will going to Raoult's law which is also a very important law to understand the properties of mixture. So, let us come to know Raoult's law.

Now, consider a simple 1 component 2 phase mixture in a thermodynamic equilibrium as shown here.

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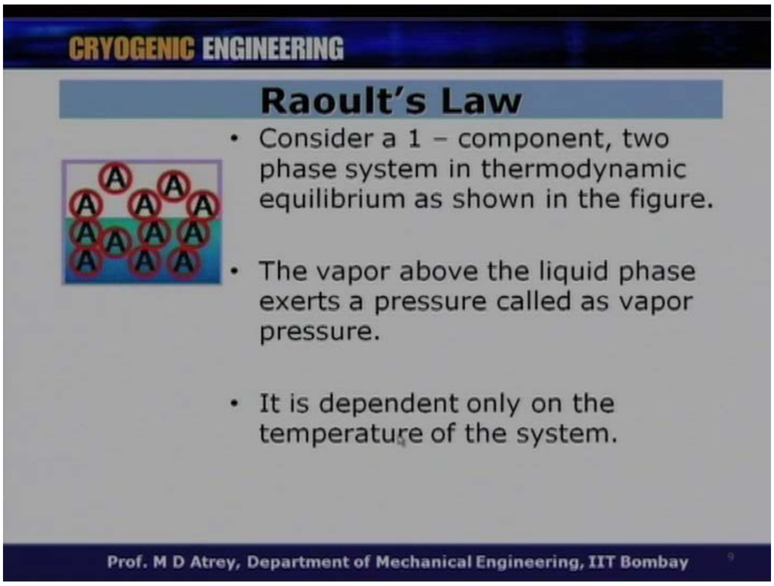

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Raoult's Law

- Consider a 1 – component, two phase system in thermodynamic equilibrium as shown in the figure.
- The vapor above the liquid phase exerts a pressure called as vapor pressure.
- It is dependent only on the temperature of the system.

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So, again in a enclosure we got a 2 phase system; that means, we have the some liquid the component is A or a Gas A and we got a some liquid which has only Gas A as a component we will have some vapor pressure basically we will have some Gas A component above this liquid in a enclosure.

So, what you have is basically a 2 phase mixture in a thermodynamic equilibrium each other, but it is a 1 component mixture it is not a mixture actually, it is a 1 component system which has got only Gas A as a component.

The vapor above the liquid phase exerts a pressure and this is called as vapor pressure, as you know a simple vapor pressure basically is a function of the temperature. So, I find out the temperature, I can compute the vapor pressure for a 2 phase system.

So, as I just said it depends only on the temperature of the system if I know the the temperature entropy diagram I can compute, if I know the temperature I can find out on a dome what is my saturated vapor pressure at that point on a dome this will give me the vapor pressure of that component for a given temperature. We will see this a again in tutorials later.

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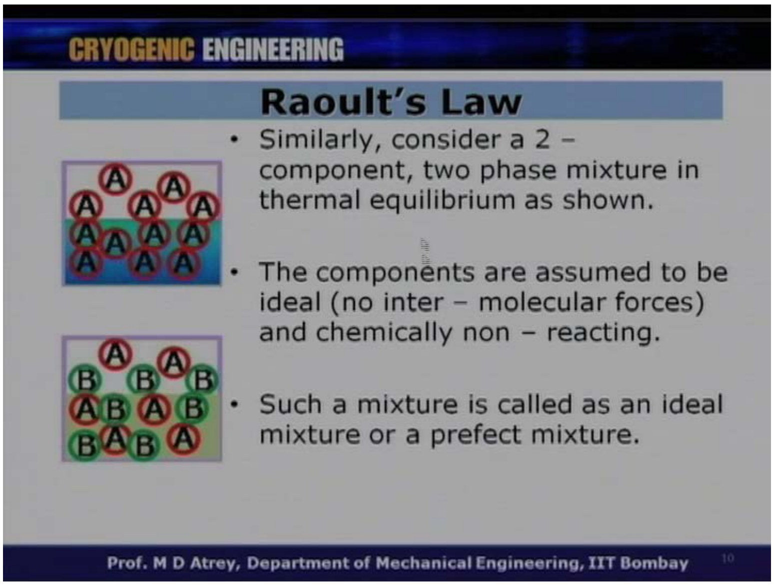

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Raoult's Law

- Similarly, consider a 2 – component, two phase mixture in thermal equilibrium as shown.
- The components are assumed to be ideal (no inter – molecular forces) and chemically non – reacting.
- Such a mixture is called as an ideal mixture or a prefect mixture.

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So, similarly now we have just seen a system of 1 component, let us now looK At the system of 2 components and 2 phase mixture in thermal equilibrium as shown. So, here you can see the upper illustration is only for gas for component A, but now I have got 2 components here which are A and B and again it is a 2 phase system and therefore, this both the components are in liquid phase as well as on a vapor phase above the liquid and they exert a vapor pressure on this liquid.

So, there in thermodynamic equilibrium with each other, but it will have different vapor pressure depending on the temperature of the mixture. So, the components are assumed to be ideal; that means, there is no inter molecular forces and chemically non-reacting.

So, non-reacting is a case must, but what is important in ideal consideration is, there is no inter molecular forces. Such a mixtures is called as an ideal mixture or a perfect mixtures in a Raoult’s law basically holds good for perfect mixture or ideal mixture.

The real mixture will deviate away from the Raoult’s law and therefore, this deviation has to be understood because in the real mixture, we will have inter molecular forces and this have to be considered, if you want to really compute to a very high degree of real analysis, if you want to do in that case, we will have to take into consideration all the inter molecular forces. It is clear that the vapor above the liquid has both the components. So, in liquid condition also we have got A and B in a vapor condition also we will have A and B.

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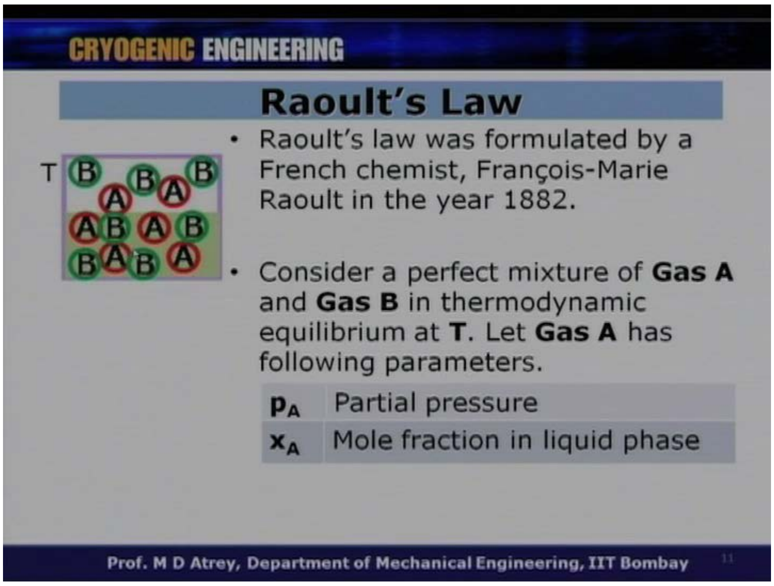

Raoult's Law

- Raoult's law was formulated by a French chemist, François-Marie Raoult in the year 1882.
- Consider a perfect mixture of **Gas A** and **Gas B** in thermodynamic equilibrium at **T**. Let **Gas A** has following parameters.

p_A	Partial pressure
x_A	Mole fraction in liquid phase

The Raoult's law was formulated by a French chemist, François Marie Raoult in the year 1882. So, this law also is a very old law almost a year 130 years or something like that and this law also has been applied over a period of time and therefore, its important has been well understood.

So, consider a perfect mixture of Gas A and Gas B in thermodynamic equilibrium at temperature Tand let Gas A has following parameter. So, the parameter associated with Gas A are p A which is this partial pressure, x A is a mole fraction in liquid phase.

Now, you have got a liquid phase coming into its now in a Dalton's law we talked only about the the gas mixture itself. Now we are talking about both liquid and vapor over here and therefore, the component what we identify in liquid is x A. So, x A is a mole fraction in liquid phase, while y A is a mole fraction in the vapor phase. So, because we have got both the phases over here we have got a concepts of x and x A and y A.

Similarly, we will have x B and y B for Gas B, we will not talk about that right now we are talking about only Gas A and by A is a very important parameter we have just talked about this also earlier which is a vapor pressure at temperature T.

Now, this is not for a mixture, we are talking about this is independent or a characteristic of any component for a Gas A if we know temperature, we know the vapor pressure at that particular temperature. So, pi A is the 1 which gives me vapor pressure of Gas A at temperature T all right.

So, we have got a four component which is the partial pressure mole fraction in liquid phase mole fraction in vapor phase and pi A is a vapor pressure at temperature T. Now basically I would like to relate all this things not only for Gas A, but for Gas B also. How do I relate them Raoult's law relate this parameter and therefore, let us see that in next slide.

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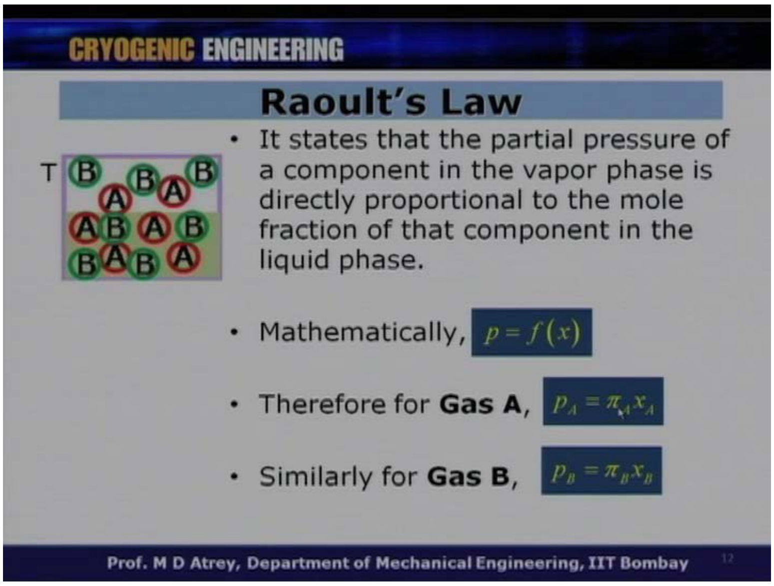

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Raoult's Law

- It states that the partial pressure of a component in the vapor phase is directly proportional to the mole fraction of that component in the liquid phase.
- Mathematically, $p = f(x)$
- Therefore for **Gas A**, $p_A = \pi_A x_A$
- Similarly for **Gas B**, $p_B = \pi_B x_B$

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So, the statement of Raoult's law is that the partial pressure of a component in the vapor phase is directly proportional to the mole fraction of that component in the liquid phase. So, what is a partial pressure of a component in vapor phase is p A. and this is directly proportional to the mole fraction of that component in liquid, we just found that x A is the mole fraction of that component in liquid phase.

So, basically the Raoult's law relates the partial pressure in the vapor phase which is of this component let us say Gas A above the liquid. The vapor pressure will be for only for the vapor which is above the liquid and vapor pressure exerted by Gas A or Gas B is related to the mole fraction of that component in the liquid phase.

So, vapor pressure p A is going to be related to x A, x A is the mole fraction of that component in the liquid phase. So, my mathematical statement therefore, becomes p is a function of effects which is what we just talked, which is p is a partial pressure and function of x and what is x? x is a molar fraction of that component in the liquid phase.

So, for Gas A now if I apply this law for Gas A I will get p A is equal to pi A x A. Its clear here p A is related to x A and what is that constant of proportional at T, it is the vapor pressure at that temperature, at the mixture temperature.

So, p A is equal to pi A x A is a very important result as to which is coming out from this Raoult's law statement, I am relating the partial pressure of a vapor in a given mixture to the molar fraction of that component in liquid phase and it is basically getting related by the vapor pressure of Gas A, which is the characteristic pressure at given temperature of mixture. So, if I know x A, I can compute its partial pressure exerted by the vapor of that component in a given mixture or in a given enclosure at temperature T.

Similarly, for Gas B if I plot the same rule for Gas B, I will get partial pressure exerted by vapor component B on this mixture of A and B and its related to the component x B and correspondent the gas the value of pi will be pi B which is the vapor pressure of Gas B at a temperature T this is a very important relationship between x A and p A and x B and p B.

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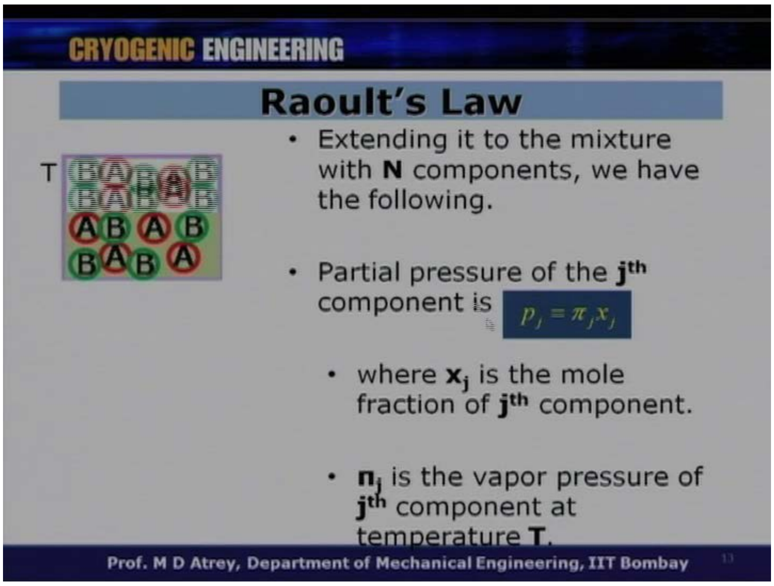

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Raoult's Law

- Extending it to the mixture with **N** components, we have the following.
- Partial pressure of the $\mathbf{j}^{\mathbf{th}}$ component is $p_j = \pi_j x_j$
  - where $\mathbf{x_j}$ is the mole fraction of $\mathbf{j}^{\mathbf{th}}$ component.
  - $\boldsymbol{\pi_j}$ is the vapor pressure of $\mathbf{j}^{\mathbf{th}}$ component at temperature **T**.

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Extending it to the mixture with n components we have just seen, what is the value of p A and what is the value of p B. If I talk about N components I will have partial pressure of j th component given as p j is equal to pi j x j, same thing not A and B anymore, but I am applying basically for any j th component if you have got n number of components in a given mixture where x j is the mole fraction of the j th components pi j is the vapor pressure of j th component at temperature Tit is clear I am just generalizing what we studied earlier.

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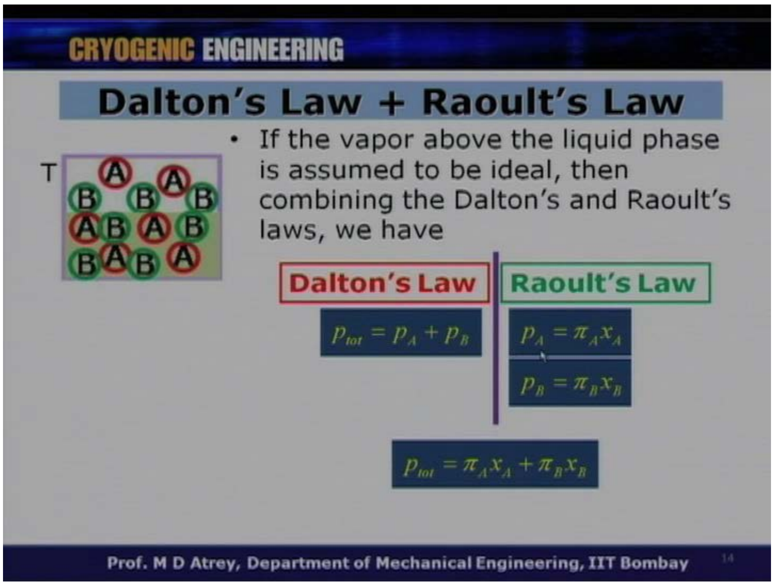

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Dalton's Law + Raoult's Law

- If the vapor above the liquid phase is assumed to be ideal, then combining the Dalton's and Raoult's laws, we have

Dalton's Law

$p_{tot} = p_A + p_B$

Raoult's Law

$p_A = \pi_A x_A$

$p_B = \pi_B x_B$

$p_{tot} = \pi_A x_A + \pi_B x_B$

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Now, we have just studied Dalton's law, we have now studied Raoult's law. If we combine both the laws for a given mixtures what we get is a very important relationship now if the vapor above the liquid phase is assumed to be ideal because you know Dalton's law is basically meant for gases, vapor is not gas, but if I assume that vapor above the liquid phase is assumed to be ideal, then combining the Dalton's law and the Raoult's law what we get is a 2 things. I will just put in Dalton's law I will then combine with it with the Raoult's law.

If I say Dalton's law what I know is the p total is equal to p A plus p B, the total pressure is equal to the sum of the partial pressure which is p A plus p B and what I get from Raoult's law is the value of p A and p B.

So, p A is equal to pi A x A and p B is equal to pi B x B where x A and x B are the molar fraction in the liquid of component A and component B respectively, while pi A and pi B are the vapor pressure of those gases at a given temperature.

So, now I can basically relate the p total to this p A and p B taking the value from p A and p B. So, what my expression will be. So, p total, I will just this p B, p A by pi A x A plus pi B x B.

So, now what I am doing is basically I am relating the total pressure to the x A and x B respectively to the molar fraction of component A and component B in a given mixture in the liquid x A and x B.

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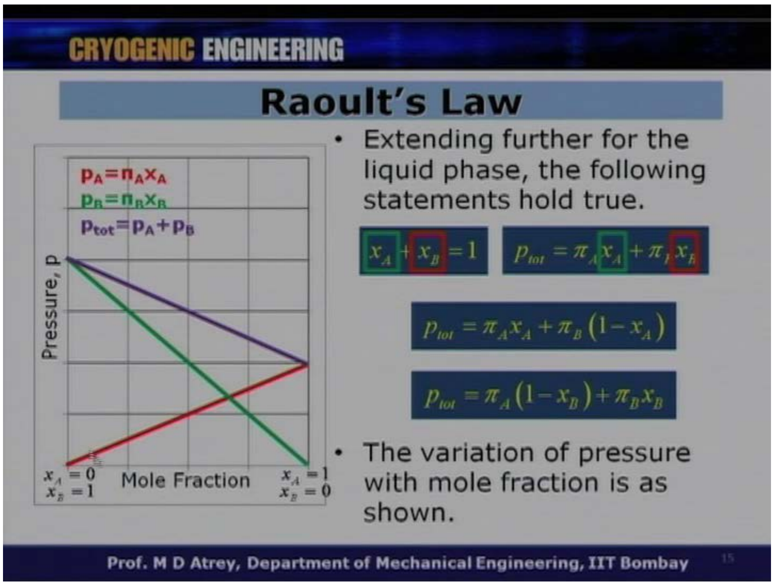

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Raoult's Law

- Extending further for the liquid phase, the following statements hold true.

$$\boxed{x_A} + \boxed{x_B} = 1 \qquad p_{tot} = \pi_A \boxed{x_A} + \pi_B \boxed{x_B}$$

$$p_{tot} = \pi_A x_A + \pi_B \left(1 - x_A\right)$$

$$p_{tot} = \pi_A \left(1 - x_B\right) + \pi_B x_B$$

- The variation of pressure with mole fraction is as shown.

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So, extending further for the liquid phase, the following statements now holds good which is we know that, x A plus x B is equal to 1. The molar fraction sum in a given mixture is going to be equal to 1 and p total what we have just seen is equal to pi A x A plus pi B x B.

If I just now replace this x B is equal to 1 minus x A and put it here, this expression what I get is p total is equal to pi A, x A, plus pi B into 1 minus x A obvious and therefore, I can do the other y is also I can put x A is equal to 1 minus x B in the same statement.

So, my p total is equal to pi A into 1 minus x B plus pi x B, I am just replacing the value of x B in this expression and the value of x A in this expression. And now I would like to put this graphically and this is what in short the Raoult's law will be.

So, you can see that I have got 2 axis on which the p is mentioned and I have got 2 end points of x axis on which I have given a mole fraction of x A. So, if I go from x A is equal to 0 to x A is equal to 1, which is 100 percent a and I have got x B is equal to 0 and x B is equal to 1, here at 2 ends at in between values I have got some value of x A for example, here I have got x A is equal to 0.25 and x B is equal to 0.75.

Here I have got x A is equal to 0.5 x B is equal to 0.5 here at the end I have got x A is equal to 1 and x B is equal to 0; that means, 100 percent a exits over here 100 percent b exits over here.

What I am plotting on this is basically p A and p B. So, p A is nothing, but pi A x A which is given in a red color over here. So, the vapor pressure partial pressure of p A at A is equal to 0 is going to be 0, while A is equal to 1 is going to be maximum. So, p A ranges from 0 to p A max here.

Similarly, the partial pressure of b will range from 0 to max here. And the total is at every point is p A plus p B. So, I did 2 end points the total pressure is equal to in fact, p A is equal to 0 and therefore, p total at this point will be equal to p B, while the p total at this point will be equal to p A and at an every intermediate point will gets algebraic sum of this vertical heights which is given by p A plus p B and this is my p total.

So, p total at every point is going to be sum of the partial pressures of p A and p B which is what what we have understood from Dalton's law and Raoult's law. So, these in actually this graphical representation of the Raoult's law and the Dalton's law all right.

So, I think just to understand in graphical form at this will help and values of p A and p B are related to x A and x B by the Raoult's law which is what we just saw. So, going ahead from here I have got 1 more law actually just deviation of the Dalton's law it is called as gobs Dalton's law.

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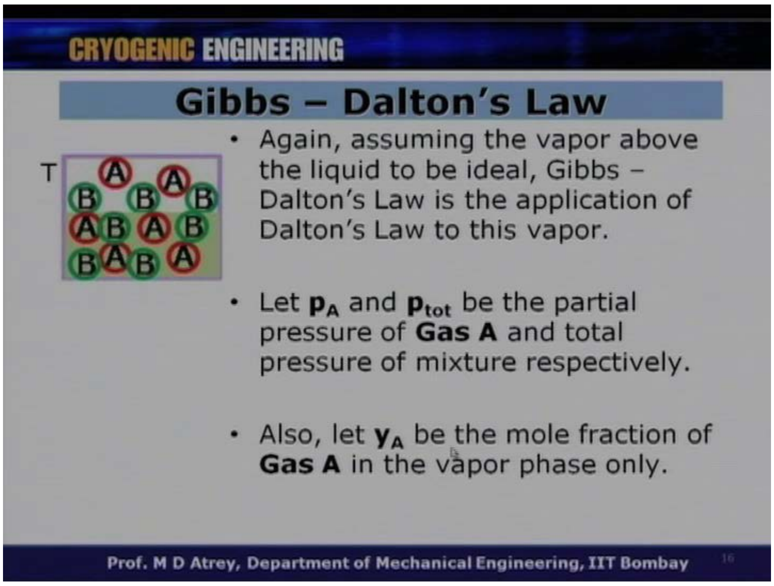

Gibbs – Dalton's Law

- Again, assuming the vapor above the liquid to be ideal, Gibbs – Dalton's Law is the application of Dalton's Law to this vapor.
- Let $\mathbf{p_A}$ and $\mathbf{p_{tot}}$ be the partial pressure of **Gas A** and total pressure of mixture respectively.
- Also, let $\mathbf{y_A}$ be the mole fraction of **Gas A** in the vapor phase only.

Again, assuming the vapor pressure above the liquid to be ideal this is what we did earlier also Gibbs Dalton's law is application of Dalton's law to this vapor, but is this showing basically I am applying Dalton's law for this vapor assuming that the vapor above are behaving ideally like ideal Gas basically. So, Gibbs Dalton law is nothing, but application of Dalton's law to this vapor.

So, let p A and p total be the partial pressure of Gas A and total pressure of the mixture respectively which is what we have seen earlier also, let Y A is the mole fraction of Gas A in a vapor phase which is what we have same nomenclature has been used as what we have done earlier.

The application of Dalton's law to the vapor above the liquid we have following now was what we are doing now basically relating p A to y A as that what we have done earlier.

For a Gas A in a vapor phase, what we know is p A is equal to p total into y A; this is what we have done. The partial pressure of Gas A is related to its molar fraction in the vapor phase and is the constant of proportional; that means p total. So, p A is equal to p total into y.

Similarly, for Gas B in the vapor phase we write p B is equal to p total into y B, this is what we have done earlier Gibbs Dalton's law is basically applying the same thing assuming that the vapor behaves as ideal gas.

Extending this to the n component mixture and for the j th component what we know is a p j is equal to p total into y j, this is the same thing applied for j th component in a n component mixture.

Now, if I combine Gibbs Dalton's law and Raoult's law together to the vapor above the liquid phase, I get the following. So, if I go by Gibbs Dalton's law I have got p A is equal to y A into p total, and the Raoult's law tell me that p A is equal to pi y A x A.

So, here I am applying the law for the vapor here I am applying the law for the liquid component. So, understand that ultimately I am relating the vapor component y A to x A which is the liquid component is a very important law therefore, I will get the vapor composition I will get the liquid composition for gas component A.

So, from here I get y A is equal to pi A upon p total into x A or pi A x A upon p total or it is a very important thing that I am relating y A which is the vapor component, vapor fraction of Gas A and x A is a molar fraction in the liquid component in the component A in liquid form. So, basically I am relating y A and x A.

Similarly, for B component we got a p B is equal to y B into p total and correspondingly Raoult's law gives me that p B is equal to pi B, x B exactly on the same line as what we did for component A. So, if I relate this thing to y B now I will get y B is equal to pi B x B upon p total. So, basically again I am relating y B and x B, in this case.

So, if I just summarize whatever laws we have studied and then we can go ahead from there the Dalton's law relates partial pressure of non-reacting ideal gases Raoult's law relates the vapor pressure with the liquid mole fraction of a component.

The Gibbs Dalton's law application of Dalton's law to the vapor above the liquid phase and we found that p A is equal to p total into y A is basically applied to the vapor now, assuming that the vapor is behaving like a ideal Gas. And lastly what we did was we combined Raoult's law and Gibbs Dalton's law together and it establish a relationship between the vapor and the vapor liquid fraction of a component this is very important law because ultimately we wanted to come to this that y A is getting related to x A.

Now, going ahead from here we define much more constant now which are very very important from mixture perspective. As derived earlier consider an equation with y A and x A for Gas A, which is y A is equal to pi A, x A upon p total.

Rearranging this, what we get is y A upon x A, is equal to pi A upon p total, what is pi, is a vapor pressure of component A at a given temperature T of a mixture what is p total, is a total pressure of the mixture. So, actually to say they are basically both constant for a given temperature and pressure of a mixture.

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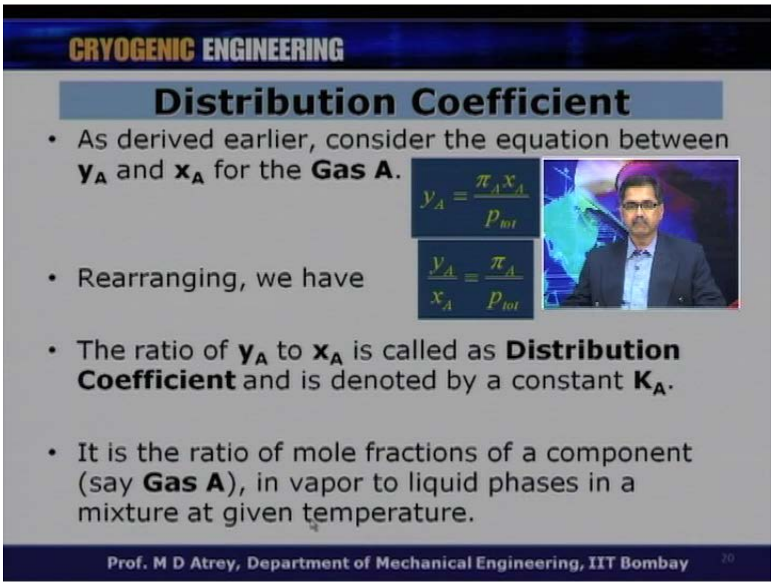

CRYOGENIC ENGINEERING

Distribution Coefficient

- As derived earlier, consider the equation between **y_A** and **x_A** for the **Gas A**. $y_A = \frac{\pi_A x_A}{p_{tot}}$
- Rearranging, we have $\frac{y_A}{x_A} = \frac{\pi_A}{p_{tot}}$
- The ratio of **y_A** to **x_A** is called as **Distribution Coefficient** and is denoted by a constant **K_A**.
- It is the ratio of mole fractions of a component (say **Gas A**), in vapor to liquid phases in a mixture at given temperature.

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See, if I know the temperature of mixture, if I know the total pressure of a mixture y A and x A the ratio of Y A and x A essentially remains a constant as long as the temperature and the pressure of the mixtures are defined.

So, what we can understand from here is for a given temperature and pressure, I got y A upon x A coming as constant and this is a very important finding.

So, the ratio of y A x A, y A to x A is basically a constant and it is called as distribution coefficient, it distributes at a given temperature the value of A in vapor phase and the proportion or molar fraction of A in a liquid phase and this is called as distribution coefficient and is denoted by constant as K A similar value we have a power B and x B also which will denoted as K B.

But what is important to understand that y A and x A have a ratio which is y A upon x A called as distribution coefficient and given as K A. If I want to define that thing it is the ratio of the mole fraction of a component, let say Gas A in vapor to liquid phases in a mixture at a given temperature.

So, if I know the temperature if I know the pressure of a mixture then y A upon x A at a given temperature is called as distribution coefficient and constant, its constant given by K A similarly, I will have value of K B.

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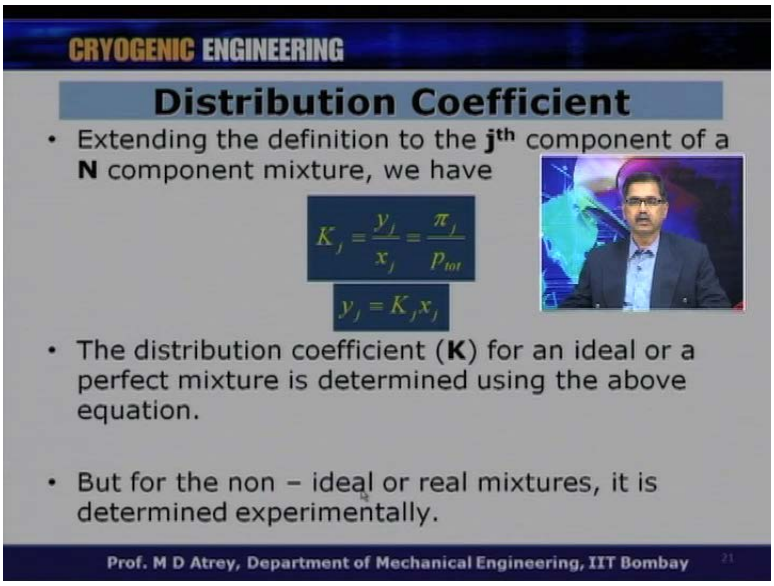

CRYOGENIC ENGINEERING

Distribution Coefficient

- Extending the definition to the **j**th component of a **N** component mixture, we have

$$K_j = \frac{y_j}{x_j} = \frac{\pi_j}{p_{tot}}$$

$$y_j = K_j x_j$$

- The distribution coefficient (**K**) for an ideal or a perfect mixture is determined using the above equation.
- But for the non – ideal or real mixtures, it is determined experimentally.

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So, extending general to the j th component I have got a K A and I have got a K B and if I go for a K j for example, for n component mixture I will have K j is equal to y j upon x j and this is equal to pi j upon p total. So, pi j is a vapor pressure of a j th component at a temperature T, p total is a mixture pressure basically given as p total.

So, again this is going to be distribution coefficient for the j th component which is going to be constant. So, y j is equal to K j s j which is what we know the distribution coefficient K for an ideal or a perfect mixture is determined using the above equation.

So, if I know if I know the temperature, if I know the pressure, I can calculate the K j value and this is an ideal or a perfect mixture, as I say the Raoult’s law basically holds good for ideal mixture or a perfect mixture or perfect solution where in there are no inter molecular forces acting.

But the non-ideal or real mixture it is determined experimentally. So, there is the 2 ways of doing that thing 1 is to get experimental values which are also distribution coefficient obtained experimentally or by empirical correlations while one can calculate based on the ideal gas or etcetera ideal, assuming that there are no inter molecular forces and therefore, one can get the distribution coefficient theoretically also.

We got one tutorial later to study, if you calculate the value of distribution coefficient theoretically and also experimentally and compare this 2 values and therefore, you'll be able to see what different does it make, if I calculate it theoretically and if I get the value experimentally.

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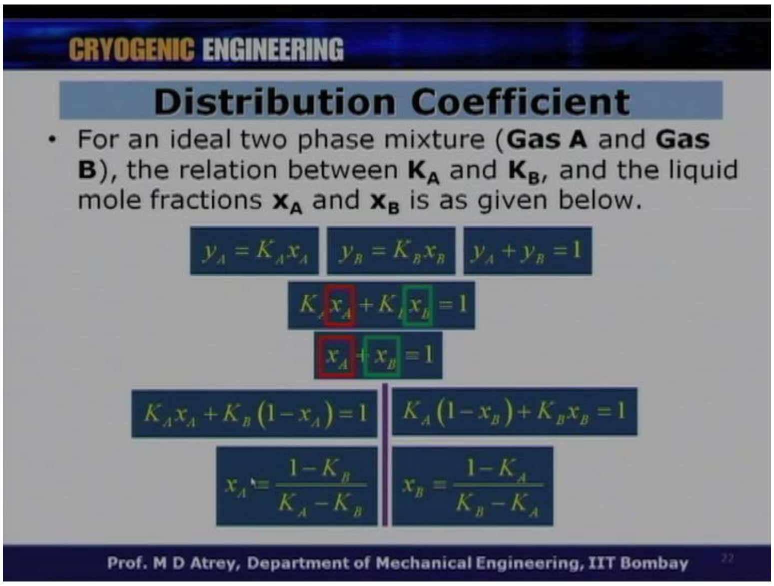

CRYOGENIC ENGINEERING

Distribution Coefficient

- For an ideal two phase mixture (**Gas A** and **Gas B**), the relation between $\mathbf{K_A}$ and $\mathbf{K_B}$, and the liquid mole fractions $\mathbf{x_A}$ and $\mathbf{x_B}$ is as given below.

$$y_A = K_A x_A \qquad y_B = K_B x_B \qquad y_A + y_B = 1$$

$$K_A \boxed{x_A} + K_B \boxed{x_B} = 1$$

$$\boxed{x_A} + \boxed{x_B} = 1$$

$$K_A x_A + K_B (1 - x_A) = 1 \qquad K_A (1 - x_B) + K_B x_B = 1$$

$$x_A = \frac{1 - K_B}{K_A - K_B} \qquad x_B = \frac{1 - K_A}{K_B - K_A}$$

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So, now for an ideal 2 phase mixture wherein we have got a Gas A and Gas B the relationship between K A and K B also has to be made clear So, K A and K B also get related and the liquid mole fraction x A and x B. So, ultimately I want to like to relate in given mixture where Gas A and Gas B are present, how are K A and K B are related to x A and x B. Because their having a mixture they will basically contribute to the calculation of value of x A which is the molar fraction of Gas A in a liquid phase and x B is the liquid mole fraction of the component B.

So, how would I do that I know y A is equal to K A x A, I know y B is equal to K B x B and I know that y A plus y B is equal to 1, see if I apply the same law for vapor we have already have done that for x A we know x A plus x B is equal to 1 similarly, we know that y A plus y B is equal to 1 and y A and y B values are given over here.

So, if I write K A plus K A x A I just replace this K y A by K A x A and y B by K B x B I know K A x A plus K B x B is equal to 1 and this is what relates the value of K A and K B and x A x B. So, we also know that x A plus x B is equal to 1 and if I therefore, replace the value x B here as 1 minus x A I get K A x A plus K B into 1 minus x A is equal to 1 and therefore, from here I can compute the value of x A is equal to 1 minus K B upon K A minus K B.

See if I know the distribution coefficient of Gas A and Gas B that is K A and K B for a given temperature and pressure of a mixture then I can compute theoretically what is the value of x A.

Similarly, I can do the same thing for x B also here if I put x A is equal to 1 minus x Bin the above expression I replace this value of x A as 1 minus x B and compute this I will get the expression for x B Which is x B is equal to 1 minus K A upon K B minus K A.

If I know the distribution coefficient for K B and K A i can compute for a given temperature of pressure what are the values of x A and x B Respectively by this formulae.

So, very important thing theoretically I will know the value of K A and K B i can compute those value other side earlier, theoretically or I can get the value of K A and K B which are available the experimental data is available for a given mixture in that case, I can theoretically compute what the value of x A and x B will be there for a given temperature in a mixture.

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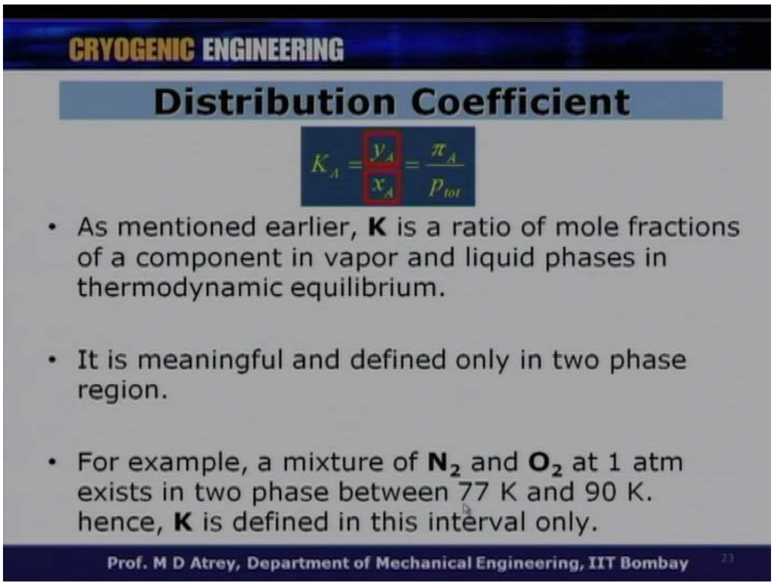

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Distribution Coefficient

$$K_A = \boxed{\frac{y_A}{x_A}} = \frac{\pi_A}{p_{tot}}$$

- As mentioned earlier, **K** is a ratio of mole fractions of a component in vapor and liquid phases in thermodynamic equilibrium.
- It is meaningful and defined only in two phase region.
- For example, a mixture of $\mathbf{N_2}$ and $\mathbf{O_2}$ at 1 atm exists in two phase between 77 K and 90 K. hence, **K** is defined in this interval only.

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So, the distribution coefficient K A is equal to y A upon x A which is equal pi A upon p total as mentioned earlier K is the ratio of the mole fraction of a component in vapor and liquid phases in thermodynamic equilibrium. This is what we have defined K As it is meaningful and defined only to 2 phase region.

Normally K A is given when component Gas A and Gas B will be together and they only there is the, their basically requirement to calculate the x A and x B, y A and y B respectively for a mixture. So, normally the values are going to be defined from the mixture component Gas A and Gas B in a 2 phase region; that means, from boiling point of A up to the boiling point of B above which there is no component left as it is basically. So, we define it normally at a given pressure between the 2 boiling points and therefore, the 2 phases the regions.

For example the mixture of Nitrogen and Oxygen at 1 atmosphere exists in 2 phases between 77 Kelvin and 90 Kelvin, the boiling point of Nitrogen and the boiling point of Oxygen at 1 atmosphere.

Hence normally the K is defined in this interval only. The same thing could b at 1 atmosphere or 5 atmospheres or whatever pressure which talk about and correspondent to those pressures will have the boiling points of Nitrogen or Oxygen or component A and component B and K value will be defined during that temperature range.

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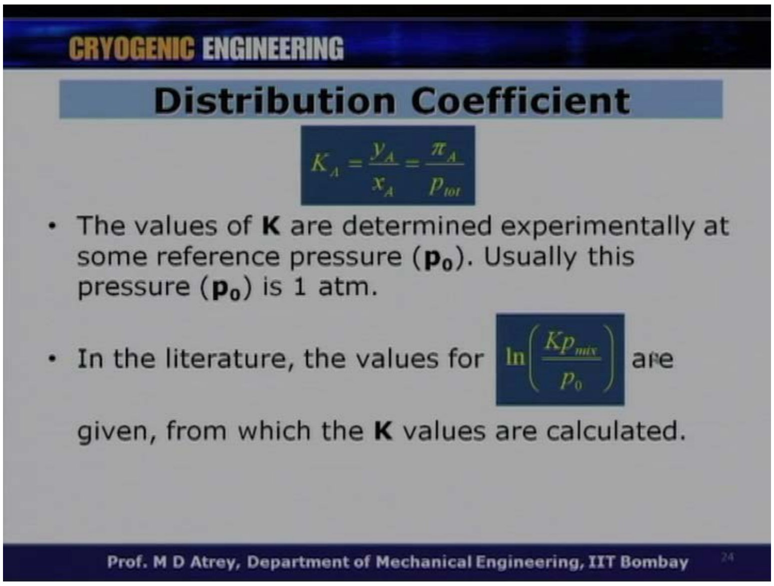

Distribution Coefficient

$$K_A = \frac{y_A}{x_A} = \frac{\pi_A}{p_{tot}}$$

- The values of **K** are determined experimentally at some reference pressure (**p_0**). Usually this pressure (**p_0**) is 1 atm.
- In the literature, the values for $\ln\left(\frac{Kp_{mix}}{p_0}\right)$ are given, from which the **K** values are calculated.

The values of K are determined experimentally a t some reference pressure p O now when I talk about experimentally determination of this values of K which is normally given with a reference pressure p O which could be 1 atmosphere, 2 atmosphere or 5 atmosphere and whenever this values are given the value of p O will be given to you and therefore, your actual mixture pressure could be different which which is just p Or p mixture, but the values will be given for that pressure with some reference pressure which has to be taken into account to calculate the value of K.

So, on the literature the values of K are normally given in logarithmical form and it is always given in this form log of K into p mixture upon p O which means that if my mixture pressure is 1 atmosphere to the value 1 over here and if I having p O also is defined as a reference point is 1 atmosphere then this 2 will get cancel in that case the p mixture is going to be is equal to p O and the log K value will be given in the table in that case.

So, normally it is given in the logarithmic form, from which and once we know this logarithmic form value the value of K has to be recalculated from this expression So, this is what the experimental values will be given, understand that tables are available which I will show you in the next slides.

The data for Nitrogen, Oxygen and Argon are given in the next slide and a tutorial has been solved later to understand this conceptually. So, how does this data look like the data is given in log K p mixture upon p O for Oxygen, Nitrogen as given below. So, this is what you can see. So, I have got a data for Nitrogen which is at 1 atmosphere p O is 1 atmosphere; that means, my reference pressure is 1 atmosphere similarly, I have got data for Oxygen again the reference pressure is 1 atmosphere.

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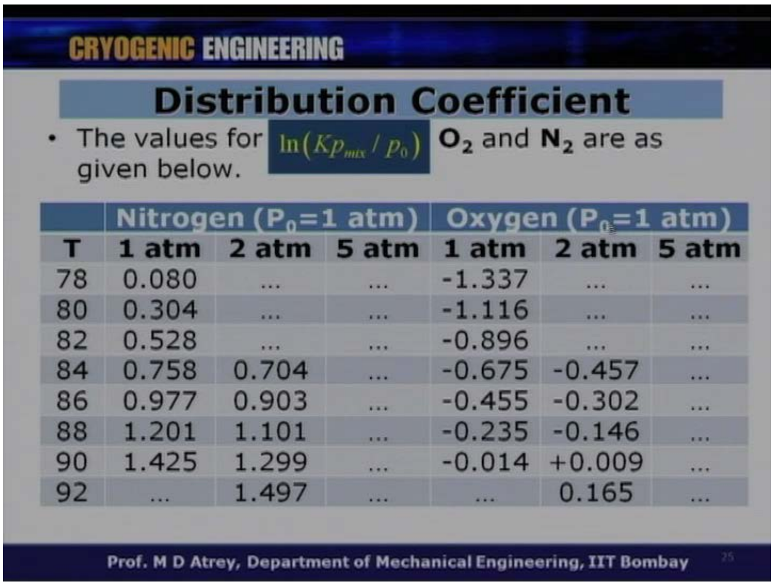

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Distribution Coefficient

- The values for $\ln(Kp_{mix} / p_0)$ O_2 and N_2 are as given below.

	Nitrogen (P_0=1 atm)			Oxygen (P_0=1 atm)		
T	**1 atm**	**2 atm**	**5 atm**	**1 atm**	**2 atm**	**5 atm**
78	0.080	...	...	-1.337	...	...
80	0.304	...	...	-1.116	...	...
82	0.528	...	...	-0.896	...	...
84	0.758	0.704	...	-0.675	-0.457	...
86	0.977	0.903	...	-0.455	-0.302	...
88	1.201	1.101	...	-0.235	-0.146	...
90	1.425	1.299	...	-0.014	+0.009	...
92	...	1.497	...	...	0.165	...

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However my mixture can be arrive from 1 atmosphere, 2 atmosphere, 5 atmosphere and whatever I have just shown 1, 2 and 5 and correspondent to this mixtures, now I have got a temperature range as i said the temperature range for 1 atmosphere will be from 77.4 to let say 90, because that happens to the boiling point of Nitrogen and Oxygen respectively.

So, the data is given as ranging from around 77 to 90 and as you can see that the high boiling component when it goes on to low boiling component basically this nothing but representative value of y by x.

So, as you see that as you go from high boiling component to low boiling component the vapor component y by x go on less and less and therefore, the value of y by x or logarithmic value goes on getting reduced and normally what we have found is around the boiling point it comes nearly to somewhere around 1 which is what we can see later.

Similarly, this value have been given for 2 atmosphere normally at 2 atmosphere the boiling point of the Nitrogen will get increased and therefore, the table is may given from 84 onwards which may go up to 94 which may happen to the boiling point of Oxygen at 2 atmosphere the boiling point does not figure in this range for 5 atmosphere. So, it comes in the next page.

Similarly, for Oxygen what we can see is this values are basically logarithmic values as less than for 1 atmosphere in this case for Oxygen because its below its boiling point the logarithmic value happens to be in a negative nature; that means, the values are less than 1 in this case. The values of K are normally around 1 at the boiling point which is what we will see later.

The values of K happened to be around 1. So, whenever there are negative points they happened to be less than 1 in that case. So, at 2 atmosphere again I will different table I got a 5 atmosphere because the boiling point get raised I have got a different table.

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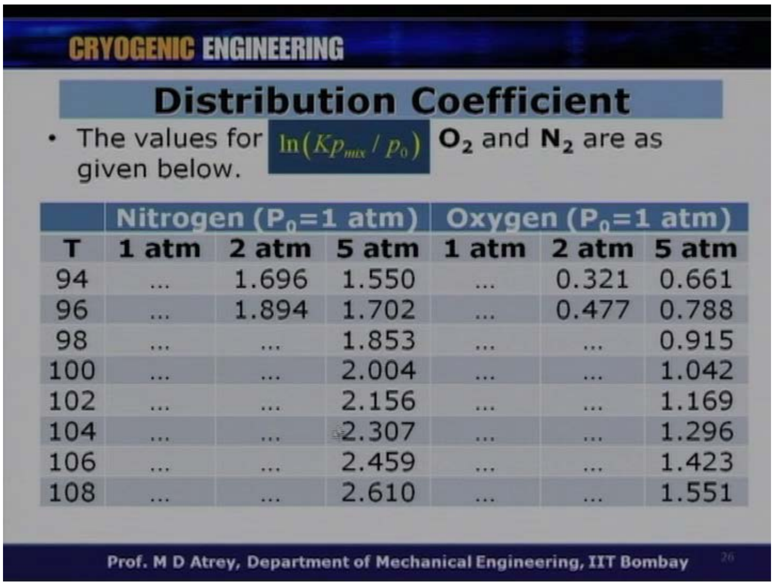

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Distribution Coefficient

- The values for $\ln(Kp_{mix}/p_0)$ **O_2** and **N_2** are as given below.

	Nitrogen (P_0=1 atm)			Oxygen (P_0=1 atm)		
T	**1 atm**	**2 atm**	**5 atm**	**1 atm**	**2 atm**	**5 atm**
94	...	1.696	1.550	...	0.321	0.661
96	...	1.894	1.702	...	0.477	0.788
98	...	...	1.853	...	...	0.915
100	...	...	2.004	...	...	1.042
102	...	...	2.156	...	...	1.169
104	...	...	2.307	...	...	1.296
106	...	...	2.459	...	...	1.423
108	...	...	2.610	...	...	1.551

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So, here we can see that the 5 atmosphere figures in a higher temperature range 94 to 108 for both Oxygen and Nitrogen respectively So, this is what the values will be given as if I just want to again similar thing is shown for Argon also and these values have to be taken from this table 1, 2, 5 atmosphere and I think this is for Oxygen.

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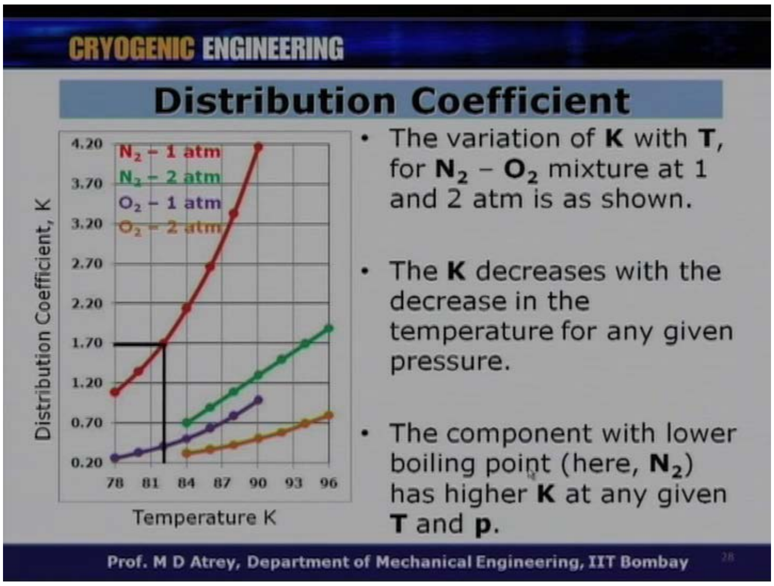

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Distribution Coefficient

- The variation of **K** with **T**, for $\mathbf{N_2}$ – $\mathbf{O_2}$ mixture at 1 and 2 atm is as shown.
- The **K** decreases with the decrease in the temperature for any given pressure.
- The component with lower boiling point (here, $\mathbf{N_2}$) has higher **K** at any given **T** and **p**.

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So, if I want to just show it as a value of K what you have seen in a table was logarithmic value, but if I want to show this on a graph it is just the value of K with temperature at different pressure. See if I say Nitrogen at 1 atmosphere you can see this is the red line and this ranges from 90 Kelvin up to its boiling point which is 77 Kelvin.

And you can see that at 1 atmosphere at 77 Kelvin the value of Nitrogen or value of K at 77 is hitting around 1, while it has gone up to 4.2 at 90 Kelvin similar thing holds good for Oxygen atmosphere, where you can see that Oxygen value at around 90 Kelvin coming closer to 1.

While below 90 Kelvin as I said earlier, it is coming less than 1 and therefore, the logarithmic value of K will be shown as negative which is what we have seen earlier. If I go for Nitrogen 2 atmosphere, because at Nitrogen 2 atmosphere, the boiling point will be increased and therefore, it will possibly go from 84 Kelvin up to 96 Kelvin and in between around this point, around 90 or 84 will come the value equal to 1, which happens to the boiling point of Nitrogen at 2 atmosphere.

If I apply the same thing for 2 atmosphere Oxygen now it will range from 84 and go up to 96 and around these, what will have is a boiling point of Oxygen at 2 atmosphere. And below that the value of logarithmic value is going to be shown as negative or the value of K is going to be less than 1.

So, this is just to give well understanding of what is the comparative value of K At different temperatures and pressure the as I said the thumb rule is if you are near the boiling point of that, but corresponded that pressure of of Nitrogen or Oxygen it is going to be around 1, below that is going to be less than 1, above the boiling point is going to be more than 1 and the logarithmic value of this less than 1 is going to be shown as negative in this case.

So, variation is shown here for Nitrogen, Oxygen we found that the K decreases with the decrease in the temperature for any given pressure. So, decrease the temperature, decrease the value of K. The component with lower boiling point has higher K. So, this clear that because of the boiling point being the minimum in this case, the values of Nitrogen the K values of K for Nitrogen is going to be more as compare to other gases in this particular expression.

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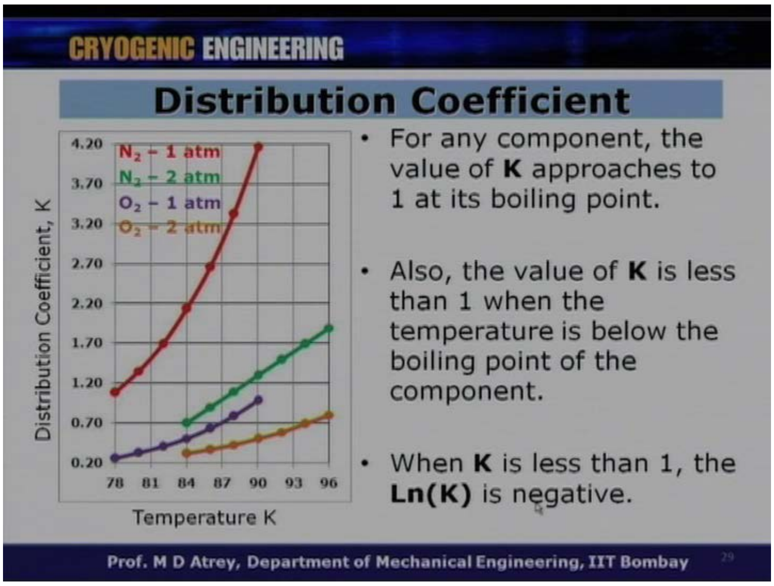

CRYOGENIC ENGINEERING

Distribution Coefficient

- For any component, the value of **K** approaches to 1 at its boiling point.
- Also, the value of **K** is less than 1 when the temperature is below the boiling point of the component.
- When **K** is less than 1, the **Ln(K)** is negative.

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For any component the value of K approaches to be 1 for a given boiling point for its boiling point. Also the value of K is less than 1, when the temperature is below the boiling point of 1. This is what I just talked, that below 77 Kelvin the value of K is going to be less than 1 or it is going to be logarithmic value is going to be negative in this case.

So, when K is less than 1, the logarithmic value of K is negative and that is what we saw in the table. So, with this background whatever we have understood till now, about the concept of y A x A, the distribution coefficient K A, K B in a given mixture of Gas A and Gas B. In order to clear some concepts, I would like to take 2 tutorials and once you solve this you will lot of concept will get clear.

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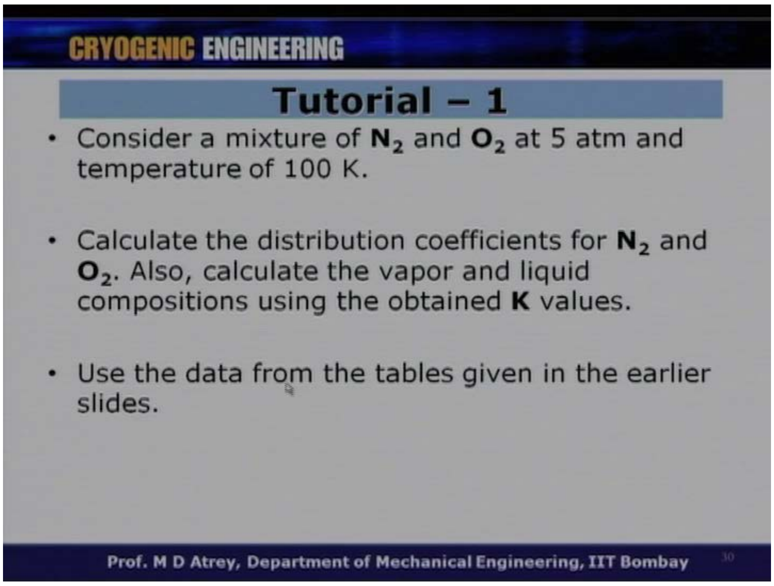

CRYOGENIC ENGINEERING

Tutorial – 1

- Consider a mixture of $\mathbf{N_2}$ and $\mathbf{O_2}$ at 5 atm and temperature of 100 K.
- Calculate the distribution coefficients for $\mathbf{N_2}$ and $\mathbf{O_2}$. Also, calculate the vapor and liquid compositions using the obtained **K** values.
- Use the data from the tables given in the earlier slides.

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So, my tutorial 1 is consider a mixture of Nitrogen and Oxygen at 5 atmosphere and temperature is 100 Kelvin. The mixture temperature is 100 Kelvin the mixture pressure is 5 atmospheres what I want to calculate calculate a distribution coefficient of Nitrogen and Oxygen, also calculate the vapor and liquid composition using the obtained K values.

So, basically I want to calculate a distribution coefficient, I don’t want to take it from the given table I want to calculate that and also once you know the value of K calculate the vapor and liquid compositions using the values of K. That is the problem. Use the data from the table given in the earlier slide.

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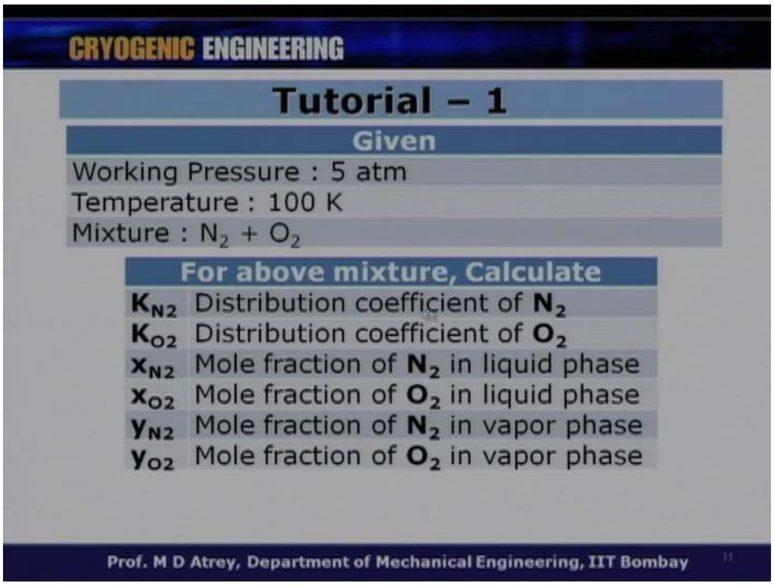

CRYOGENIC ENGINEERING

Tutorial – 1

Given

Working Pressure : 5 atm
Temperature : 100 K
Mixture : $N_2 + O_2$

For above mixture, Calculate

K_{N2}	Distribution coefficient of N_2
K_{O2}	Distribution coefficient of O_2
x_{N2}	Mole fraction of N_2 in liquid phase
x_{O2}	Mole fraction of O_2 in liquid phase
y_{N2}	Mole fraction of N_2 in vapor phase
y_{O2}	Mole fraction of O_2 in vapor phase

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So, working pressure is 5 atmosphere, temperature is 100 Kelvin mixture is Nitrogen, Oxygen. This is what the problem definition; this is what the problem is given as. So, what do I want to calculate, if I want to convert that to my understanding of the nomenclature which we have been using till now is, I would like to calculate K N 2 which is distribution coefficient of Nitrogen, I would like to calculate K O 2, which is the distribution coefficient for Oxygen, which is what we talked as K A and K B earlier. I am now want to give a values to it, I want to give the nomenclature to it, which is K N 2 and K O 2.

Also correspondent to that I have got x N 2 x O 2 which are the mole fractions Nitrogen and Oxygen in liquid phases which we are earlier called as x A and x B. Similarly, I have got y N 2 and y O 2 as the mole fractions of Nitrogen and Oxygen in vapor phases. Earlier they were called as y A and y B. So, basically I want to calculate K A, K B, x A, x B, y A, y B as K N 2, K O 2, x N 2, x O 2 and y N 2, y O 2 in this problem. And they have to be done at 5 atmosphere working pressure and temperature at 100 Kelvin.

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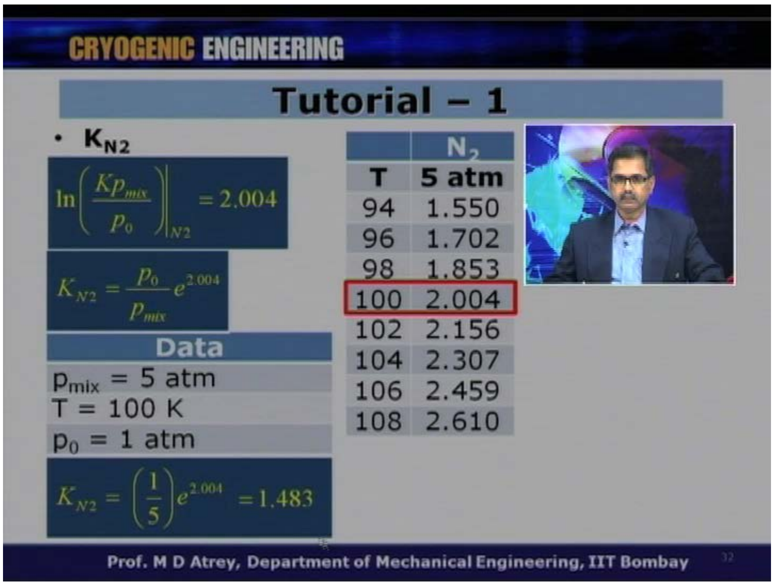

CRYOGENIC ENGINEERING

Tutorial – 1

- K_{N2}

$$\ln\left(\frac{Kp_{mix}}{p_0}\right)\Bigg|_{N2} = 2.004$$

$$K_{N2} = \frac{p_0}{p_{mix}} e^{2.004}$$

Data

p_{mix} = 5 atm
T = 100 K
p_0 = 1 atm

$$K_{N2} = \left(\frac{1}{5}\right) e^{2.004} = 1.483$$

	N_2
T	5 atm
94	1.550
96	1.702
98	1.853
100	2.004
102	2.156
104	2.307
106	2.459
108	2.610

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I first want to get the value of K N 2. So, I go for the table and get the value of K at 100 Kelvin. See, if I go to the table, I get the value of 100 K value, which is given in the logarithmic form, log of K p max p mixture upon p O for Nitrogen I go to the table I get a temperature and for 5 atmosphere and locate the value of t is equal to 100 Kelvin and this logarithmic value happens to be 2.004. Having done this for Nitrogen, I would like to calculate what is the value of K from here. So, putting the value of K into removing the logarithmic term what you get it p O upon p max, p p mixture e to the power 2.004 all right.

And then what are the values of p O and p mixture p O is 1 atmosphere p mixture is 5 atmosphere putting the value of e is 1.5 e to the power 2.004, I get the value of K N 2 as 1.483. This is my distribution coefficient for Nitrogen at 100 K and pressure of 5 atmosphere similar thing I will do for K O 2 also for the distribution coefficient Oxygen.

So, for K O 2 I take a table of Oxygen at 5 atmosphere and I will locate the 100 Kelvin in that. So, logarithmic of log of K mixture upon p O for Oxygen at 100 K and 5 atmosphere is 1.042 from where I will calculate the value of K O 2. K O 2 is given as p O upon p mixture e to the power 1.042 and putting the value of p O and p mixture in that I can again the value of K O 2 is equal to 0.567.

So, I got now K N 2, I got K O 2, once I know K N 2 and K O 2,, I will have to calculate the value of x N 2 and if I relate earlier expression I have got x N 2 is equal to 1 minus K

O 2 upon K N 2 minus K O 2 and similarly, I have got a relation for x O 2 also which I will expert in the next slide.

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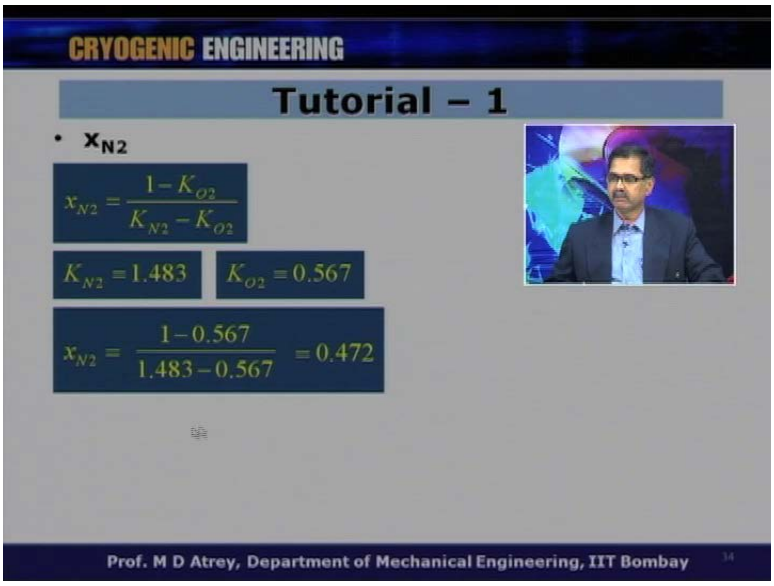

CRYOGENIC ENGINEERING

Tutorial – 1

- x_{N2}

$$x_{N2}=\frac{1-K_{O2}}{K_{N2}-K_{O2}}$$

$K_{N2}=1.483$ $K_{O2}=0.567$

$$x_{N2}=\frac{1-0.567}{1.483-0.567}=0.472$$

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So, once I know the 2 distribution coefficient for K N 2 and K O 2, I can calculate x N 2. Putting the value of K N 2 and K O 2 as what we have just calculated, I will get the value of x N 2 is equal to 0.472. Clear, I think it is very simple and straight forward.

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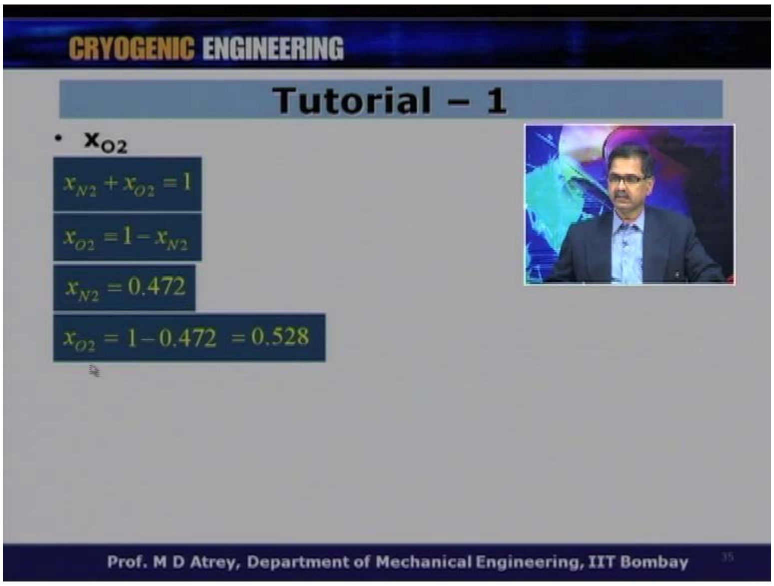

CRYOGENIC ENGINEERING

Tutorial – 1

- x_{O2}

$x_{N2}+x_{O2}=1$

$x_{O2}=1-x_{N2}$

$x_{N2}=0.472$

$x_{O2}=1-0.472=0.528$

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Having done this I can do the same thing for x O 2, where I know x N 2 plus x, x O 2 is equal to 1. So, 1 minus x N 2 will give a value of x O 2, just put those values and x N 2 is equal to 0.472 which we have just calculate to value of x O 2 therefore, is 0.528.

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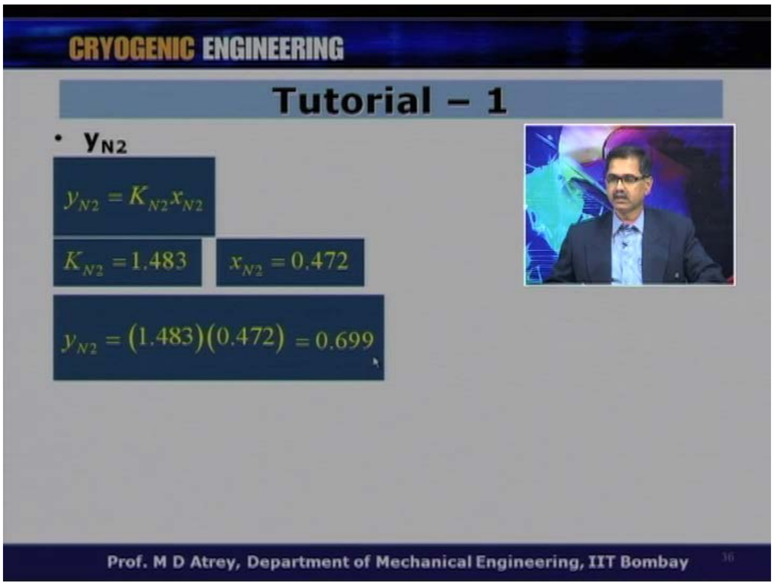

CRYOGENIC ENGINEERING

Tutorial – 1

- y_{N2}

$y_{N2} = K_{N2} x_{N2}$

$K_{N2} = 1.483$

$x_{N2} = 0.472$

$y_{N2} = (1.483)(0.472) = 0.699$

So, I have got now x N 2 and x O 2 and I will get value of y N 2 and y O 2 also that comes automatically when I know distribution coefficient. So, y N 2 related to x N 2 by y N 2 upon x N 2 is equal to K N 2. So, if I know the value of K N 2 and x N 2, I can straight away calculate the value of y N 2. So, just put 1.483 into 0.472 is equal to 0.66699 which is nothing but the y N 2 and similarly, y O 2 is nothing but we can calculate in this way also we can compute by y O 2 is equal to K O 2 you know into x O 2 which is also known to us just do 1 minus y N 2 I get y N 2 is equal to 0.699 and for y O 2 is equal to 0.304.

And therefore, I have got all the values of y O 2 and y N 2 and x O 2 and x 1 2 which is the vapor molar fraction in the vapor for Oxygen and Nitrogen and molar fraction in the liquid which is x N 2 and x O 2 which is what the total is asked for. Having done this now let go to the next tutorial, wherein we talked about a different requirement now.

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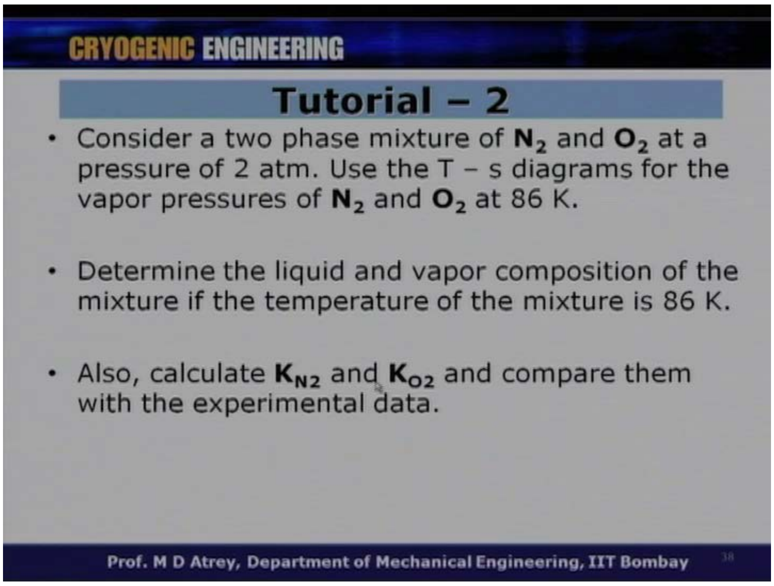

CRYOGENIC ENGINEERING

Tutorial – 2

- Consider a two phase mixture of N_2 and O_2 at a pressure of 2 atm. Use the T – s diagrams for the vapor pressures of N_2 and O_2 at 86 K.
- Determine the liquid and vapor composition of the mixture if the temperature of the mixture is 86 K.
- Also, calculate K_{N2} and K_{O2} and compare them with the experimental data.

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So, what is the next tutorial now, this is the first tutorial we just to calculation of K N 2 and K O 2, basically not calculation. Taking the value of K N 2 and K O 2 from the table and relating it to y N 2, y O 2, x N 2 and x O 2.

The second tutorial is now, consider a 2 phase mixture of Nitrogen and Oxygen again at a pressure of 2 atmosphere. Use the T-S diagram for the vapor pressures of N 2 and O 2 at 86 Kelvin. So, what I want to do is get a vapor pressures at n of N 2 and O 2 at 86 Kelvin. And determine the liquid and vapor composition of the mixture if the temperature of the mixture is 86 Kelvin.

Now, I cannot use the table. This is what is basically mentioned over here that I should use the vapor pressure of Nitrogen, Oxygen 86 Kelvin. And this is basically in order to calculate the value of K N 2 and K O 2 theoretically. As you remember in the theoretically we do not consider real gas values operate vapor as real vapor, where the no inter molecular forces are considered theoretically and that is where the this is coming from that I would not like to take a vapor pressure value of Nitrogen and Oxygen at 86 Kelvin.

Also calculate the value of K N 2 and K O 2; that means, get the value of K N 2, K O 2 from here and compare that with the experimental data the problem definition is, compute K N 2, K O 2 theoretically and compare them with the experimental available value of K N 2 and K O 2. very interesting, so, that we can understand how to calculate it theoretically which we have already seen actually in principle, how to get the K N 2 and K O 2 values and compare this values with the experimentally obtained K N 2 and K O 2 which are basically obtained from the given table earlier.

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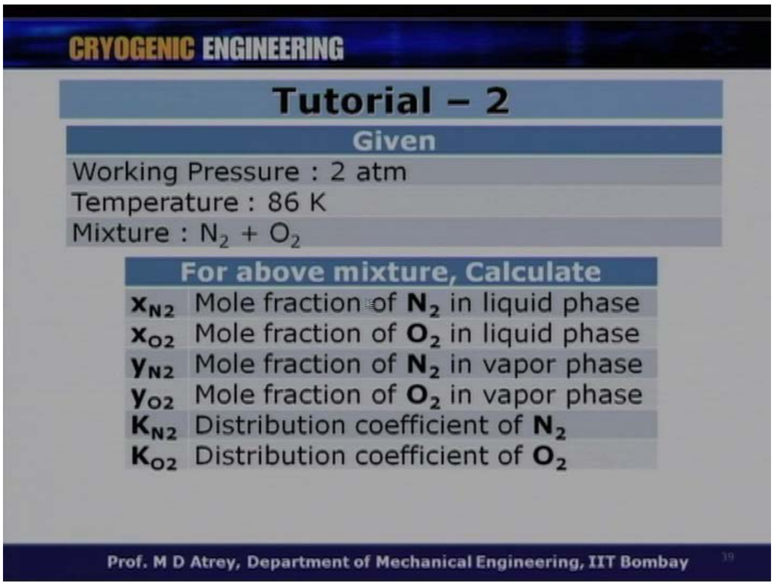

CRYOGENIC ENGINEERING

Tutorial – 2

Given

Working Pressure : 2 atm

Temperature : 86 K

Mixture : $N_2 + O_2$

For above mixture, Calculate

x_{N2}	Mole fraction of N_2 in liquid phase
x_{O2}	Mole fraction of O_2 in liquid phase
y_{N2}	Mole fraction of N_2 in vapor phase
y_{O2}	Mole fraction of O_2 in vapor phase
K_{N2}	Distribution coefficient of N_2
K_{O2}	Distribution coefficient of O_2

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So, the given is working pressure is at 2 atmosphere temperature is 86 Kelvin for a mixture of Nitrogen and Oxygen and what do I want to calculate, I want to calculate x N 2, x O 2 which is the mole fraction of Nitrogen and Oxygen in a liquid phase, y N 2 and which is the mole fraction of Nitrogen and Oxygen in vapor phase, and K N 2 and K O 2 which are the distribution coefficient of Nitrogen and Oxygen respectively, for given temperature 86 and pressure 2 atmosphere.

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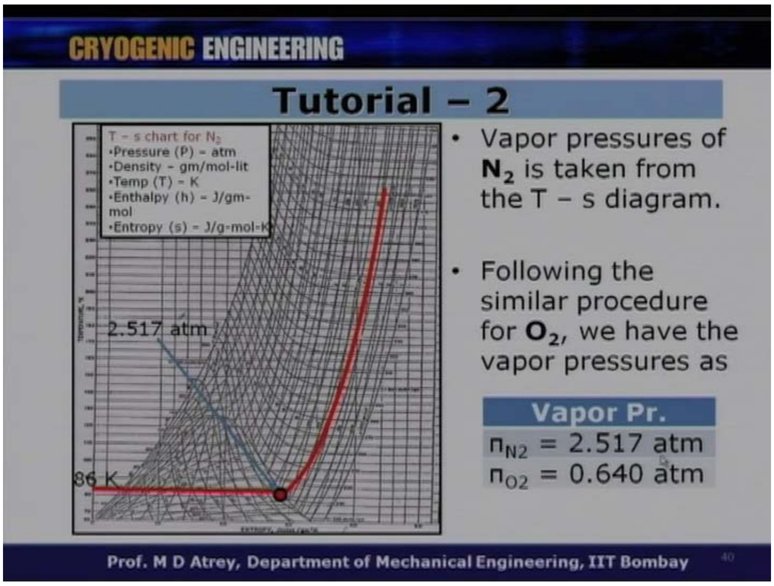
CRYOGENIC ENGINEERING

Tutorial – 2

- Vapor pressures of $\mathbf{N_2}$ is taken from the T – s diagram.
- Following the similar procedure for $\mathbf{O_2}$, we have the vapor pressures as

Vapor Pr.
π_{N2} = 2.517 atm
π_{O2} = 0.640 atm

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So, I would I go, I would I start. As I said I am told in the problem or the tutorial that I have to take a vapor pressure of Nitrogen let say at 86 Kelvin. So, correspondent to that I will get these values from the t s diagram and if I locate the temperature of 86 Kelvin in these correspondents to this value I can read the pressure.

So, this is basically saturated vapor curve. So, this is the basically two phase equilibrium that the Gas and two phase the coming vapor and the liquid are coexistent there in thermal equilibrium on this saturated vapor curve.

And therefore, wherever this horizontal line hits or intersects the saturated vapor curve correspondent to that whatever is the pressure is the vapor pressure at 86 Kelvin. And therefore, this happens to be at 2.517 atmosphere. And this is the vapor pressure of Nitrogen at 86 Kelvin and this is what I require, which is my value of pi N 2, this is the function of only temperature and the vapor will exists only up to the critical temperature of the Nitrogen.

So, therefore, vapor pressure is given normally below the critical temperature of a given component or gas. Following the similar procedure for Oxygen, we have the vapor pressure for Oxygen also which happens to be 0.64 atmosphere.

So, pi N 2 is 2.517 atmosphere and same thing is repeated for Oxygen pi O 2 is 0640 atmosphere. So, having done this I can now calculate the value of K N 2 as p total pi N 2 x N 2 pi O 2 into 1 minus x N 2, these are the values which have to be theoretically applied x N 2 therefore, is equal to algebraically I will get this values, putting this values I will get x N 2 as 0.724.

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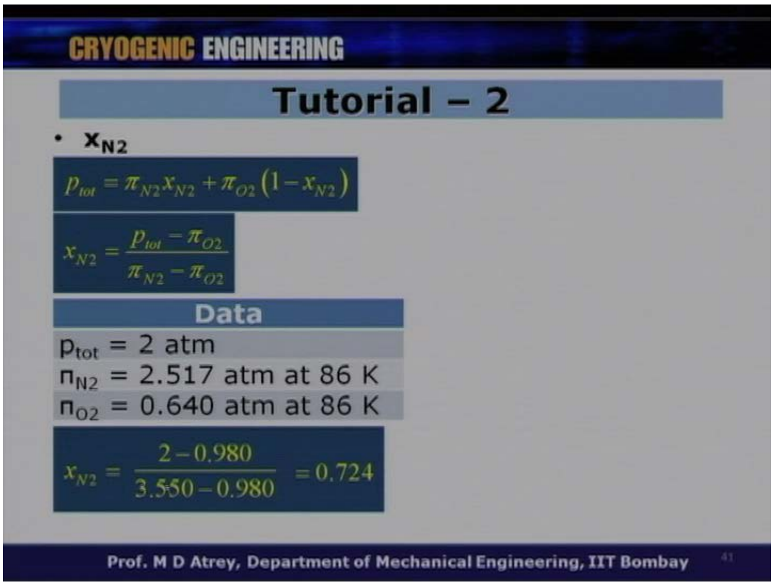

CRYOGENIC ENGINEERING

Tutorial – 2

- x_{N2}

$$p_{tot} = \pi_{N2} x_{N2} + \pi_{O2}(1 - x_{N2})$$

$$x_{N2} = \frac{p_{tot} - \pi_{O2}}{\pi_{N2} - \pi_{O2}}$$

Data

p_{tot} = 2 atm
π_{N2} = 2.517 atm at 86 K
π_{O2} = 0.640 atm at 86 K

$$x_{N2} = \frac{2 - 0.980}{3.550 - 0.980} = 0.724$$

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So, what I know is vapor pressure of Nitrogen vapor pressure of Oxygen at 86 Kelvin, I know the value of x N 2 and I can compute therefore the value of x N 2 depending on p total and the value of vapor pressures over here.

So, I get x N 2 is equal to 0.724 similarly, x O 2 is 1 minus x N 2, I get x N 2 as 0.724 and x O 2 as 0.276. I will get the value of pi N 2 in the same way where I know the total pressure, I know the pi N 2, I know the x N 2, having done this I will just put those values over here and y N 2 is calculated as 0911.

So, once I know the pi N 2 upon p total which is what we have calculated, I can relate that y N 2 with x N 2 similarly, I can get y O 2 as y N 2 plus y N 2 is equal to 1 and 1 minus y N 2 will get y O 2 and therefore, y O 2 is 0.089, I can get the value of K N 2 by just finding out the ratio of y N 2 upon x N 2 because a definition gives K N 2, putting those values over here I will get the value K N 2 to be equal to 1.2583. Understand that the value of K N 2 has been computed at 86 Kelvin which is above at volume point and therefore, value of K is more than 1, 1.25 here.

And similarly, the value of K O 2 is going to be 0.089 upon 0.276 which is 0.3224, again understand that the value of K O 2 is computed at 86 which less than its volume point and therefore, its happens to be less than 1, which is 0.3224.

So, calculated if I want to see in the value of K calculated which is y upon x and I get calculated value of K N 2 as 1.25 and K O 2 as 0.3224 and if I take the similar values from experimental now I can see the experimental values of K N 2 are 1.2335 and K O 2 is 0.36.

So, you can see there is a difference between the 2 values theoretically calculated experimentally calculated difference is not too much, but there is a difference and therefore, sometimes this experimental data can be taken, sometimes this calculated data can be taken, but it is not possible to every time, you know calculate the values because some values may not be available or it is not possible sometimes to have all the experimental data available in your table and therefore, the compromise may have to be done for given the range of temperature.

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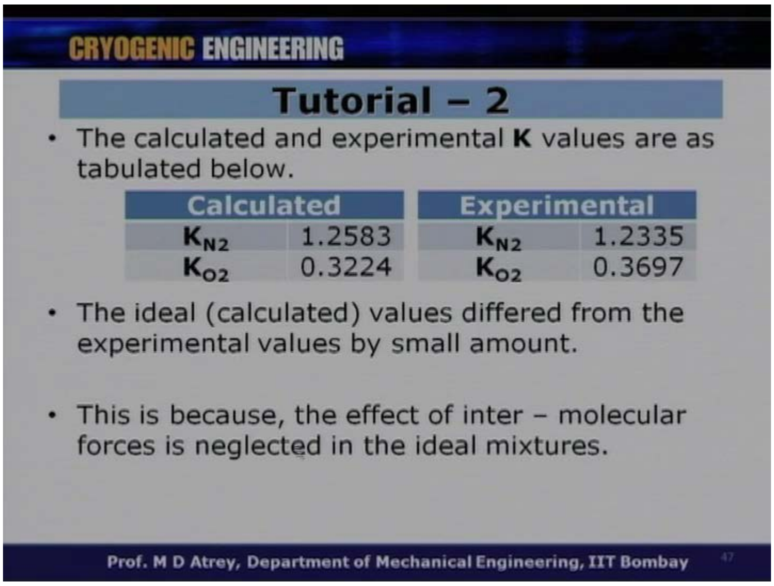

CRYOGENIC ENGINEERING

Tutorial – 2

- The calculated and experimental **K** values are as tabulated below.

Calculated		Experimental	
K_{N2}	1.2583	K_{N2}	1.2335
K_{O2}	0.3224	K_{O2}	0.3697

- The ideal (calculated) values differed from the experimental values by small amount.
- This is because, the effect of inter – molecular forces is neglected in the ideal mixtures.

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See if I compare this 2 the difference is basically going to the the ideal values differed from the experimental values by small amount and this is because the effect of inter molecular forces is neglected in the ideal mixtures and this is what i have been talking about earlier.

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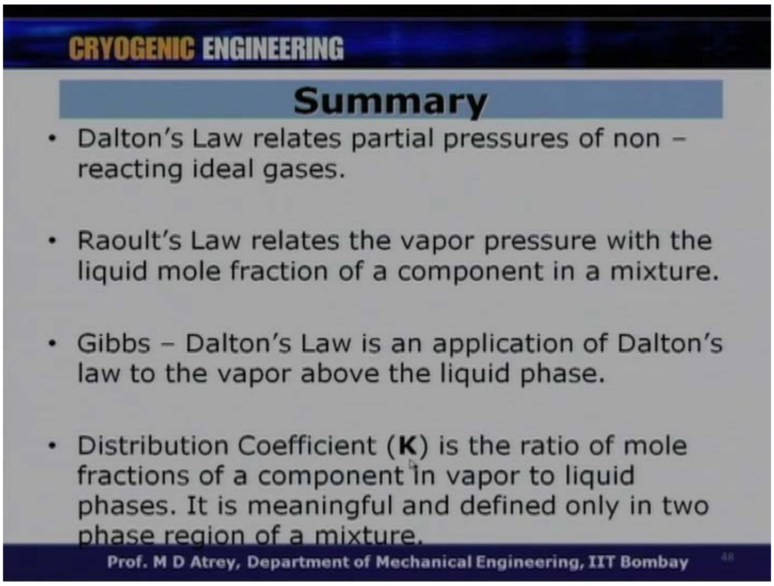

CRYOGENIC ENGINEERING

Summary

- Dalton's Law relates partial pressures of non – reacting ideal gases.
- Raoult's Law relates the vapor pressure with the liquid mole fraction of a component in a mixture.
- Gibbs – Dalton's Law is an application of Dalton's law to the vapor above the liquid phase.
- Distribution Coefficient (**K**) is the ratio of mole fractions of a component in vapor to liquid phases. It is meaningful and defined only in two phase region of a mixture.

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So, summarizing my lecture today, what we understand is Dalton's law relates partial pressures of non-reacting ideal gases. Rout's law relates the vapor pressure with the liquid mole fraction of a component in a mixture. So, y A is getting related to x A. Gibbs Dalton's law is an application of Dalton's law to the vapor above the liquid phase which is what we understood.

And we found that distribution coefficient K is the ratio of mole fractions of a component in vapor to liquid phases. So, K is equal to y by x. It is meaningful and defined only in a 2 phase region of a mixture. this is what we did.

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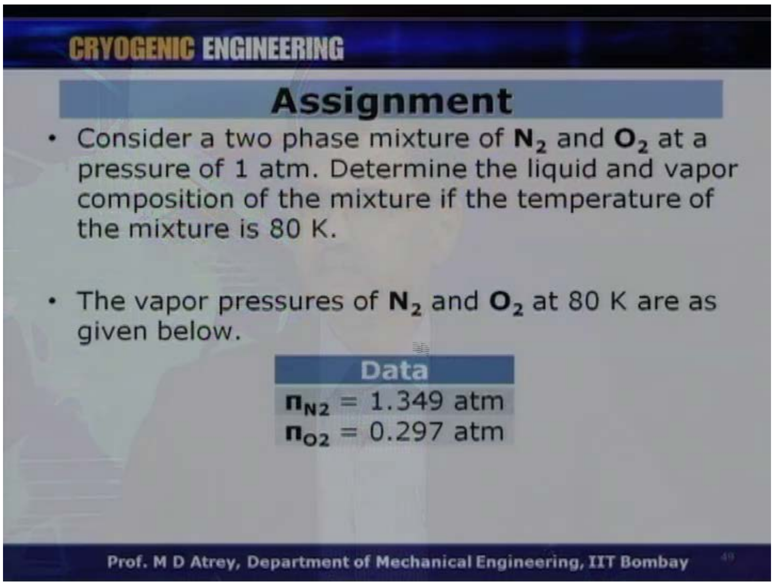

CRYOGENIC ENGINEERING

Assignment

- Consider a two phase mixture of **N_2** and **O_2** at a pressure of 1 atm. Determine the liquid and vapor composition of the mixture if the temperature of the mixture is 80 K.
- The vapor pressures of **N_2** and **O_2** at 80 K are as given below.

Data

π_{N2} = 1.349 atm

π_{O2} = 0.297 atm

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I have got a small assignment for you, which is for Nitrogen, Oxygen mixture at 1 atmosphere and at 80 Kelvin. Please find out the vapor pressure, and compare the data with experimental value, and this is the answer for that. The problem is given to you, these are the answer, please solve the problem for yourself. Thank you very much.