Engineering Thermodynamics
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Lecture – 45
Properties of Ideal Gas Mixtures: Introduction to mixtures properties

This is a Thermodynamics II, the second module in the course thermodynamics. We follow up on thermodynamics part 1 where we had studied about pure substance and various concepts and definitions associated with it.

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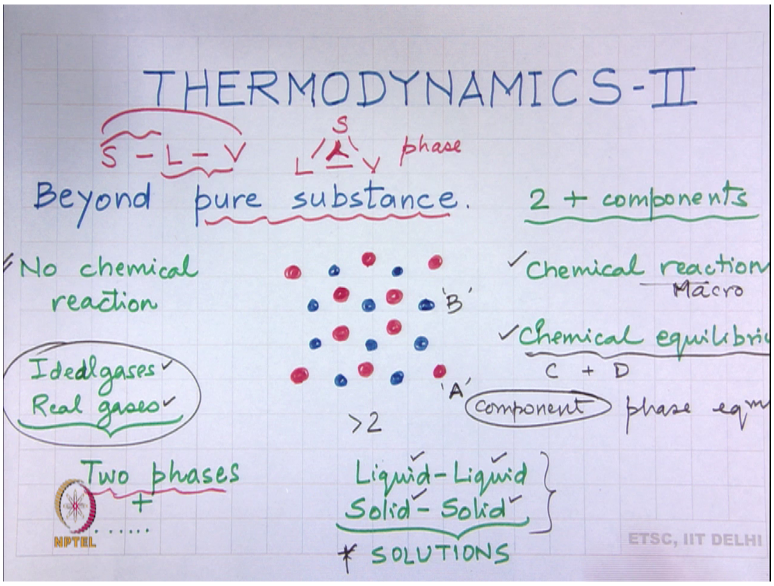

So, thermodynamics II module builds up on what has been learnt in thermodynamics I which was largely the pure substance. By pure substance we meant that this had only a single component, single type of a molecule.

So, there was no mixtures but in some sense we did look at a slightly different form in which this molecules can exist, which was to look at the phases. So, we came across the solid phase, the liquid phase and the vapour phase and we looked at systems were each one of them existed by themselves and also we looked at systems where two of these existed together in equilibrium and also where all three were in equilibrium. So, in some sense the pure substance that we studied had a possibility of three single phases, three two phase and one where all three existed together.

So, in that sense we have introduced one new concept which will be applicable in thermodynamics II which is the phases of a pure substance. So, let us see what is it that this module is all about. Now we are looking at the fact that we go beyond a pure substance and look at you have a substance where two different molecules are mixed in some form. So, here you have red ones this is one type of a molecule and we can say that this is a molecule A, and the blue once we can say this is molecule B. And the question we ask is how do we analyze systems where the working substance is not a pure substance, but a mixture like this.

So, several possibilities exist in this that you could have a mixture where both are gases, ideal gas or a real gas or both could be liquids or both could be solids. The important thing here is that irrespective of what combination is there, we are look going to look at the system where there is no chemical reaction which means that, these molecules are in equilibrium without any form of chemical reactions. So, the mixture at any time at any state only has these two types of molecules and no intermediates which could have been formed by a chemical reaction between them, no matter how small in quantity. So, that we are precluding.

Although I have shown this picture of only two types of molecules, the analysis that we will develop is not necessarily limited to 2, but it could be more than 2 also. So, you could have a mixture of three different types of molecules and the mythology that we will develop is sufficiently broad enough that we can tackle those types of situations and problems with what we are going to learn here. What we will restrict ourselves in this beginning part of this type of a course is to look at mixtures of gases only. We will not be looking at mixtures of liquid and solids which are known as solutions and these are actually left as topics for an advanced course typically aims a chemical engineering.

So, this is one of the things that we want to learn now the what is the behaviour of this type of a mixture this is what we want to know that is one. What we will also learn in the modules of this course is, if such things actually exist then is it always that there are only two types of molecules A and B. Well when you look at these substances, it could be possible that there could be a chemical reaction between them to any extent that may be possible. So, we will look at the fact that besides having mixtures where there are no chemical reactions, we will also look at mixtures where there is a chemical reaction and it goes to an end product.

So, this we will look at the macro level and ask questions like how much energy is released and what is the type of reactants that of will produce what type of what product products will produce what type of reactants. Then we will also ask the question that if we have this mixture where these molecule can react and starting from this state we make the reaction to go forward, then gradually A and B will disappear and say to other molecules say C and D will start forming.

We will also ask the question to what extent will this A and B get transform to C and D? Whatever we have learnt in school chemistry is that all of these will react and everything will go to C plus D that is how we wrote all the chemical reactions. But that is now how things happen in the real world, it is the forward reaction that goes in this direction at the same time there is also backward reaction where C plus D is going back to A plus B.

And we will ask at what condition does this forward and backward reaction attain equilibrium and that will be the composition of that particular mixture. So, this is the scope of thermodynamics II, where we will look at first multi component systems what we are calling as molecules is what we will now call as a component. And we will first look at multi component systems and how we can get their behaviour and their properties that is part 1 which we will do now. We will follow this up with one special case of two component systems which is air and water particularly in the context of air conditioning.

Then we will move on to chemical reactions and look at the macro level what happens; at then we look at chemical equilibrium and phase equilibrium, as to what is it that determines what will be formed when you mix two different substances or two different phases of the same substance. So, this is the broad plan of thermodynamics II module.

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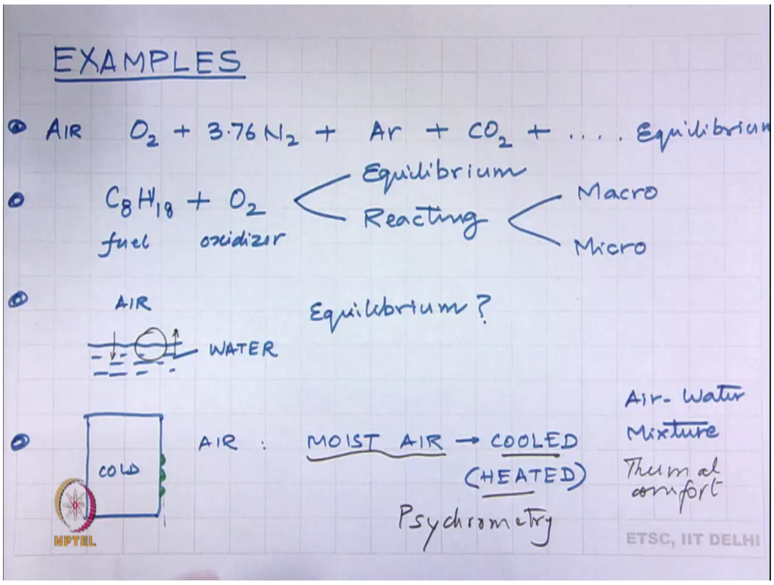

So, where do we encounter such applications or rather why do we want to study all these type of things? Here I listed some examples and the first one is about air, which we know is 25 percent by volume oxygen and 79 percent of the volume nitrogen and small amounts of argon and carbon dioxide.

With we have in thermodynamics I trigged air as some sort of a pure substance, assign certain properties to it and tackled a whole bunch of problems so that is a first cut analysis of these problems. Now when you want to become more realistic, whichever I will not treat air as a single component pure substance, but I will treat it as a mixture of oxygen and nitrogen and then let us see what happens. So, how do I handle this type of a problem that is the question we are going to answer.

Another example is if you have vapor of a fuel say in this particular case octane it could be anything, it could be natural gas say methane and it could be with an oxidizer pure oxygen or with an oxidizer which is air, oxygen plus nitrogen, then we ask the question that if I have these two this sort of a mixture and if I do nothing, will it react? What will be the equilibrium composition in that case and then suppose we do initiate chemical reaction, it begins to react and what is it that we will get in the end, at the macro level how much energy will be released that is an important thing we want to know.

And at the micro level we will ask you know what was the chemical equilibrium that produce it will get produce and what is the species that are going to be formed, not just the carbon dioxide and H 2 O that we know will come but also because the energy released the reaction between oxygen and nitrogen and how much of say nitrous oxide will be found.

So, that is the theory of that is what you also want to look at. A third application is pictured here, where you have say water in a glass or surface of ocean or a lake on which there is air which may be dry or it may have some air some water vapour in it. And the question we are asking is what is happening at the interface here, where on one side we have liquid, water and this side you have air. How much of water vapour will go in this direction and what will be the composition of air and to what extent will air go into the water and what will be the composition of that one.

We would like to know at this point only we restrict ourselves to the equilibrium behaviour of such a phenomena. Applications of this are like drawing of a fabric or a cloth, if it is wet and we have letting it dry in air the moisture or H 2 O molecules in the materials they are going out mixing with the air and then that way just the fabric would get dried up. A third another application here is a pictured a say vessel containing cold substance called I mean maybe 5 degrees 4 degrees or even containing a mixture of ice and water, sitting in ambient air. And you all know that if the air is humid which means it has got lot of moisture in it, then the water begins to condense on the outside of this vessel and begins to fall down.

So, the question that we would like to ask is, when you take moist air and cool it or heat it what happens to it? What are the properties of this air as it undergoes a heating and cooling processes? So, all of this leads to an important application of thermodynamics which is related to comfort, which is particularly thermal comfort and this is called psychrometry. So, this is important in air conditioning applications. So, the overall plan of thermo dynamics two module we can summarize it in this way.

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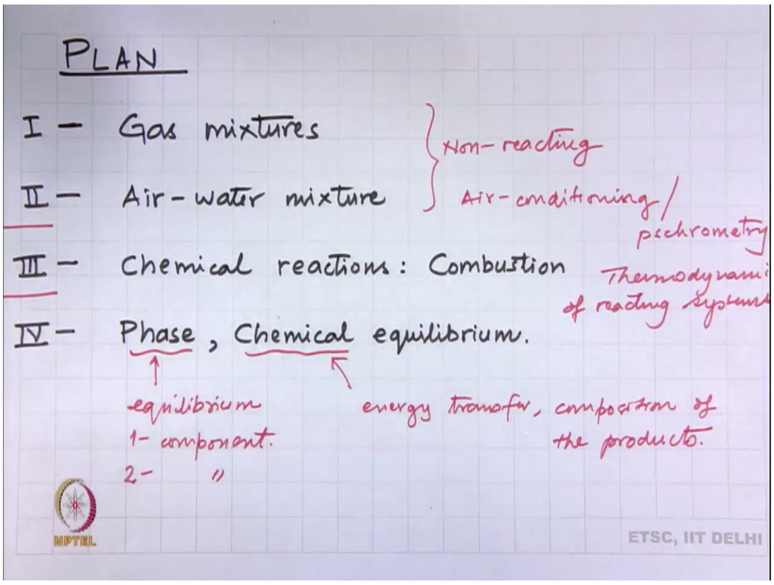

First we will look at gas mixtures and see first how to get the properties of a gas mixture and second how can we apply the laws of thermodynamics that we have learnt earlier the conservation of mass conservation of energy and the second law to a system in which there is heat transfer work transfer, but the working substance is a mixture. So, we will develop the equations for that.

This is module I of thermodynamics II. In module II we will look at air, water, mixtures which is a special class of gas mixtures and in both these cases we are looking at the mixture that is non-reacting. So, here we look concentrate that there is air in which there are smaller quantities of moisture and we ask the question how can I get the properties of this mixture and how can I predict the behaviour of the substance under different processes. This is module II which deals with air-water mixture and takes us into applications of air conditioning, and not just as far as thermal comfort goes, but also related to many industrial processes.

Another I mentioned this is what takes us into psychrometry. So, we will study the fundamentals of what happens here and see what is the format in which one can analyze such systems. So, that is the II module. In the III module we will look at reacting systems. So, we will be looking at what we will call the thermodynamics of reacting systems. So, we have a mixture fuel and oxidizer plus maybe others also and now we are consciously asking the question that, let us assume we are able to get this thing to react at the end when all the reaction is over and an equilibrium has been reached, what is the relation between the energy generated by the reaction and heat and work transfer from the system.

So, this is what we will get from the third module. In the IV module we will ask the question what is it that determines the equilibrium condition of either just a group of molecules as in chemical equilibrium or and if they are all in the same phase or if some of them are in say a liquid phase or a solid phase, then what will be the criteria for phase. So, we are looking at two things phase equilibrium, the simplest case of which is what we have learnt for a pure substance. So, one component phase equilibrium and we will also look at two components, where one of the component has got two phases.

So, what is the criteria by which we can predict what will be the equilibrium state of that is of a mixture. And chemical equilibrium the question that we will ask is after reaction is over, how can I predict the energy transfer and to some extent the composition of the products, that is the fourth module of thermodynamics II. So, we will now begin with a study of gas mixtures, this is module I of the second part of thermodynamics.

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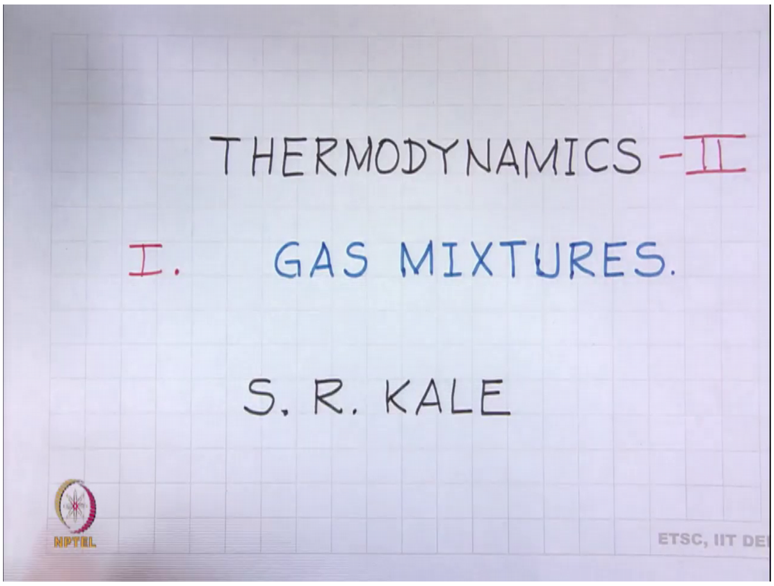

So, approach in this case is to draw upon what we have learnt from a basic thermodynamics course.

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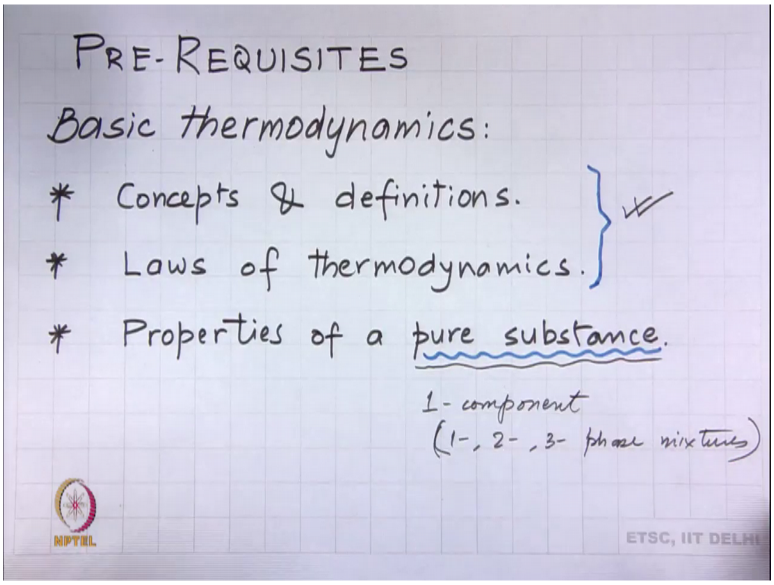

In that we started with concepts and definitions, and it was all these concepts and definitions that enabled us to make a system, look at its laws analyze those. So, that let us to the laws of thermodynamics, the 0th, 1st and the 2nd law of thermodynamics and also we looked at conservation of mass. Both these aspects were absolutely general in nature and not restricted to any particular system or any particular working substance.

We will draw upon these in what we are going to look at now for mixtures. What was different in thermodynamics I was that we took these things to a special class of problems, with a working substance was a pure substance which means 1 component. But we did not limit ourselves to only one phase, we looked at 1, 2 and 3 phase mixtures and we said what how can we predict the properties in the behaviour of such mixtures. So, what we do now is, we will draw upon both these parts from thermodynamics I and have exactly the same meaning and everything from concepts and definitions and expand that where the working substance is not a pure substance, but a mixture.

So, in the discussion I will not re derive any of these concepts, I expect that they have been studied well enough and we are applying them in the proper way in solving the problems that we are looking at. So, here is the big difference that is coming up now.

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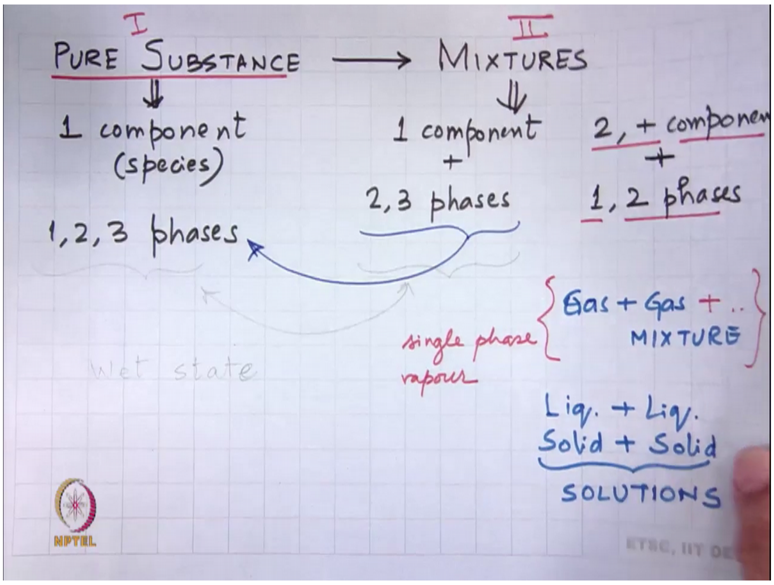

First in part I we had a pure substance, now we are looking at mixtures, but in mixtures we had one component with two or three phases, which was essentially this part essentially is the same as what we did in part I. What we are now going to look at is systems with 2 or more components with and without either all are in 1 phase or 1 or more are in 2 phases.

So, we will start with the simplest one which is to look at a gas gas mixture and we are not going to be looking at they are both gases or maybe even more gases are there if there are three component systems, but they all are in a single phase, which is the vapour phase. So, we will restrict our discussion and we will now go into depth into asking questions about a gas gas mixture or more than two component gas mixtures. We will not be looking at liquid liquid mixtures and solid solid mixtures or even combinations of that liquid plus liquid plus gas, we these are known as solutions and those are very different mode of tackling. So, we will not going to the details of this.

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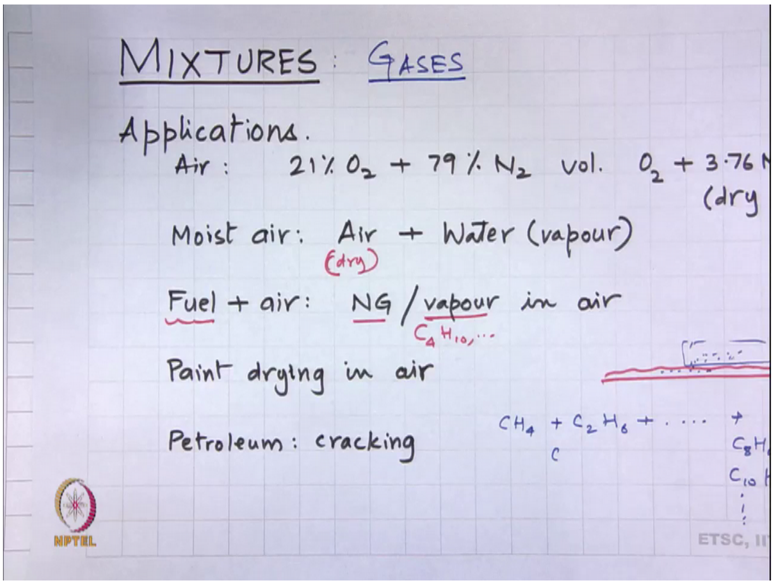

So, examples of mixtures air is 21 percent oxygen, 79 percent nitrogen by volume and if you write as a molar thing for every mole of oxygen, there is a 3.76 moles of nitrogen. And if this air has nothing else say there is no H 2 O in it we call it dry air. Then there is moist air where we have this air which we will call it say dry air, and it contains some water vapour in it all the air we breathe has different varying quantities of water vapour in it depending on the conditions and what we call as very humid climate, it we are basically saying that air has lots of H 2 O in it.

So, this is another example of a mixture, it is this type of air which is reacted with a fuel in any combustion application it could be an IC engine or an aircraft engine or like a domestic burner on which cooking is done.

So, we are looking at now air maybe dry air may be moist air, in which we have got a fuel being mixed like natural gas or vapour of any other fuel like say butane C4H10 or anything else. And this mixture you will be want to know what is the property of this mixture. At this point we will not ask the question, but what happens when it is ignited or will it burns that is out of our preview. Another example of a mixture would be say paint or some other material which has been applied with the solvent and that is drying in air.

So, we have a surface on which there is some material has been put here and what we are saying is that there are some molecules in this which have gotten out into the air and that is the drying process and we ask the question what is the property of this type of a mixture. What drives the process like this falls in a entirely different type of a subject, it is not considered here. An example where more than one molecules exist together is petroleum cracking, where when crude oil is cracked it produces a whole bunch of mixture of whole bunch of gases like CH 4 C 2 H 6 and so many more things.

So, there is some light hydrocarbons medium and then there will be heavier hydrocarbons C 8 H 18 C 10 H 22 and so on. With that some multi component mixture and we are very interested in that because we want to know how can we use knowledge of thermodynamics to separate them. So, that we have LPG coming primarily as butane something else coming out as what we call gasoline or petrol, somewhere we get diesel kerosene all of that. So, that is a very large number of components all of which add that point happened to be in the vapour phase and so we can look at mixtures.

So, we are looking at here is mixtures of gases. Many more examples one can saw it, I have given here just a flavor for why we are learning this type of a subject.

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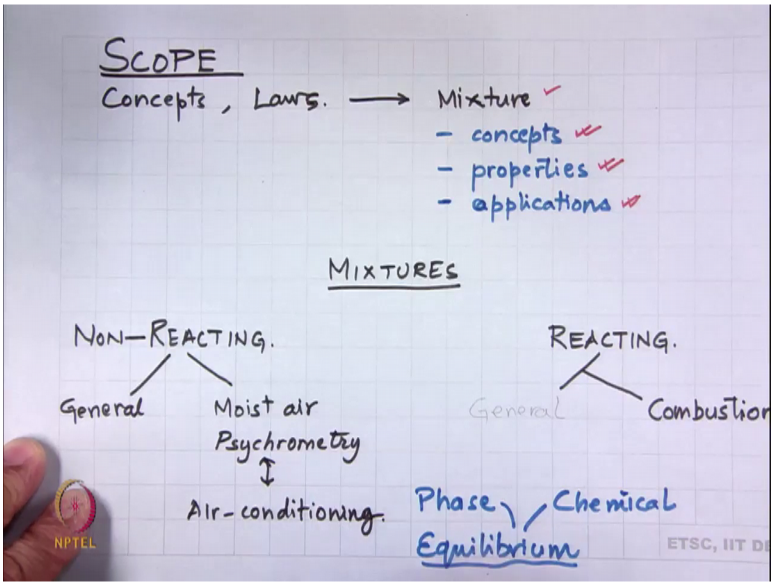

So, what we will do here is that we will start with concepts and laws extend those to mixtures, we will add some more concepts in this particular discussion, we will get to see how to get properties of mixtures and then applications.

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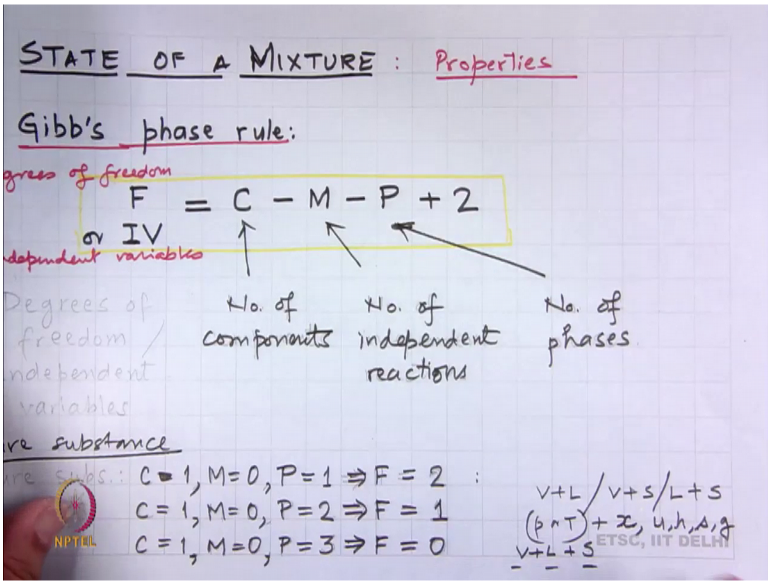

So, let us start by saying how do I quantify a mixture and we say the state of a mixture will be done as in the case of a pure substance by its properties.

And we go back to something we had come across in thermodynamics I, which is called Gibbs phase rule which says that the degrees of freedom F or independent variables IV is C minus M minus P plus 2 where C. So, this side this part of the degrees of freedom or independent variable, C is number of components, M is the number of independent reactions and P is the number of phases. So, what we have done is written down Gibbs rule in its most general form, which includes multi components, multi phase and also reactions.

So, let us look at what we have already learnt and what this thing tells us is that when you are studying a pure substance, it is single mole type of a molecule component number of components is 1, we were not looking at a reacting systems. So, M is 0 and if we say that the component existed only in one phase vapour or liquid or solid, then from this relation we get F is equal to 2. And that is what we were working with all the while that we needed to if you needed to specify the state of a pure substance which was in a single phase, then we have two independent variables that should be specified to fully quantify the state.

Now you look at the next thing that we did in pure substance, again component is 1 it does not react, but now we have two phases in equilibrium and in this case we recall we have studied vapour plus liquid equilibrium, vapour plus solid equilibrium and liquid plus solid equilibrium. So, what happens in this case is that, when you put these numbers into this equation we get F is equal to 1.

So, in that sense once you specify one property pressure or temperature lot of the other properties got fixed, but to fully specify the state we needed something else and that we said could be p or T plus another independent property once the new things that came out there were the dryness fraction x or we could have specified any of the other properties. And now look at the case which happens at the triple point, where in same single component system no reaction is taking place, number of phases is 3 this formula tells us that F is equal to 0; that means, all the properties of the phase of each phase is completely decided and there is nothing there is no variability in that.

So, this is what happens at triple point where vapour plus liquid plus solid and again the only thing that can change in this is the relative proportion of the three phases, but the pressure, the temperature are exactly the same, we now look at mixtures.

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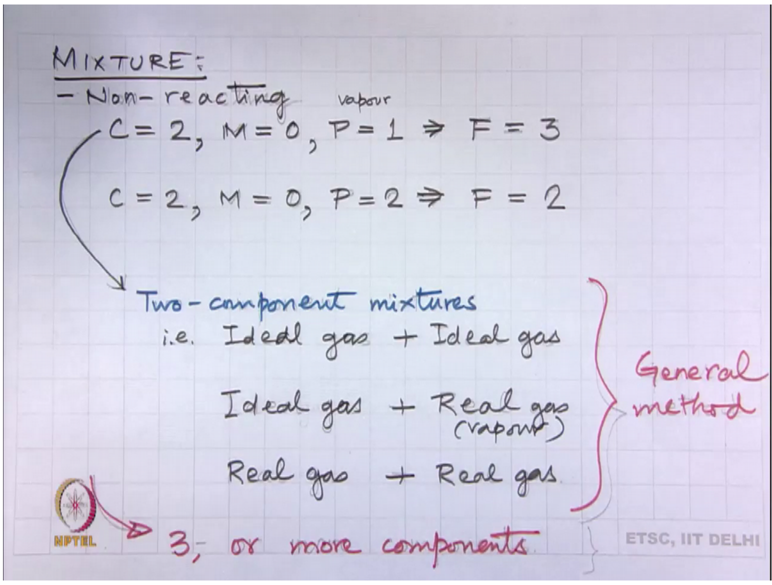

And as before to begin with we will again say that we are going to restricting ourselves to a non reacting system. And so, we say we have say two components oxygen and nitrogen in air, we are not going to look at reactions at all. So, M is 0 and both are in say vapour phase. So, number of phases is 1 and this tells us F is equal to 3.

So, we have 3 degrees of freedom that means we need to specify at least you have to specify three properties to completely specify the state of the mixture. Now if C is 2 again, no reactions M equal to 0, but one of the components has got two phases. So, like the example of water over which air is there. So, you have water vapour in the air in the vapour phase and water in the liquid form. So, you have vapour and liquid existing together in that case this tells us that F is 2. We need to look at something else beyond specifying the two properties.

What we will do now is to restrict ourselves to the first category of problems where you have a single phase and no reactions and two components. So, we are going to be studying two component mixtures and one can argue that the simplest thing to look at could be that we have one component which is an ideal gas and so is the other one. Oxygen and nitrogen in ambient air both are ideal gases or we could have an ideal gas as one of the components and a real gas or it could even be a vapour as the second component, and then we could have a mixture where both components behave like real gases. We have done this simply because analysis of ideal gases as we have learnt in the part 1 of the course is relatively easy to tackle.

But of course, limited by the fact that the substance has got to be a pure in the idea gas condition. So, although we had going to be looking at this, what we will be doing though that the method that we will start putting together now will be sufficiently general in nature, that it can be looked at for two component mixtures 3, 4, 5 anything. So, in that sense what we will learn here is good for 3 or more component mixtures.

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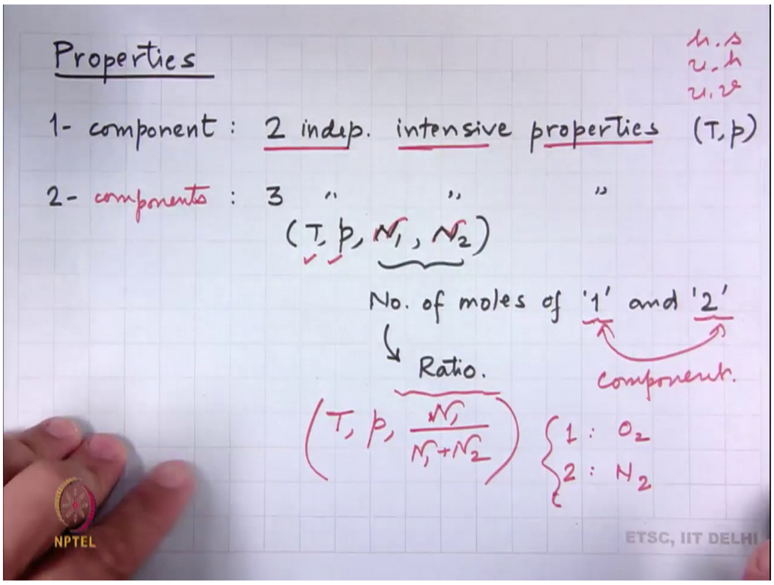

We now look at properties of a mixture for one component system we have argued earlier that you need two independent intensive properties. So, it is not necessary that it could has to be T and p, it could be u and v it could be u and h it could be h and s any combination is fine, the state is fully defined. For two component mixtures we need three independent intensive properties which could be say T and p and then now that you have two components, the simplest thing one can ask is how much is the quantity of each one of those components and that we are listed as N 1 and N 2 which is the number of moles of 1 and 2 where 1 and 2 denote the components.

So, in air component 1 could be oxygen and component 2 could be nitrogen. So, instead of giving values of both, we can give the ratio of in some form and that will give make the property and the state completely defined and some ratio of say N 1 over N 1 plus N 2 in a minute we will see how to get this particular the details of this.

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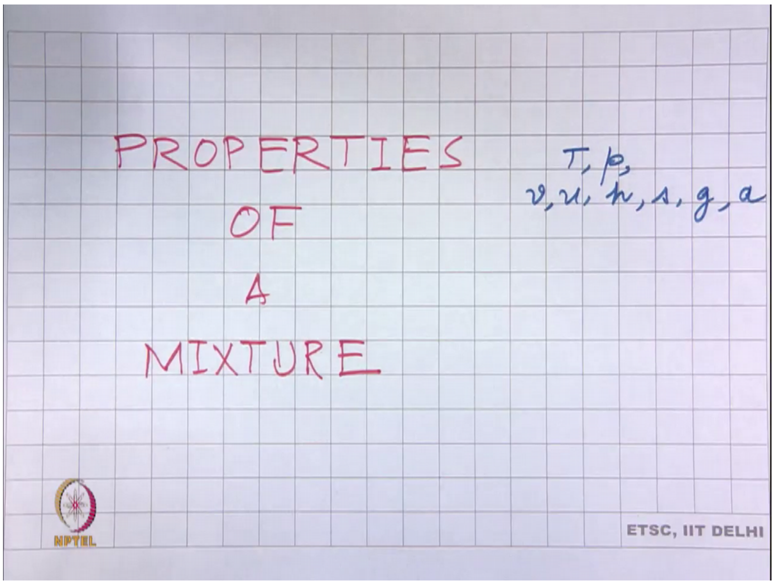

So, what we now do first is see how to get the properties of a mixture and then we will go back to the conservation of mass and energy, and see how to apply how those questions that we have earlier get modified for the case of a mixture.

So, we start with properties of a mixture. So, properties means like what we are looked at as an ideal gas we say well as pressure, there is temperature, there is densities, specific volume, specific internal energy, specific enthalpy I would like to know all those things. So, when we talk of that we is not only have T and p, but as far as we have learnt in the earlier courses this is u h s b and say g or even a Gibbs function the Helmholtz function. So, how do we get these for a mixture? And to get that we begin by asking in the what is the mixture composed of; what does the mixture contained.

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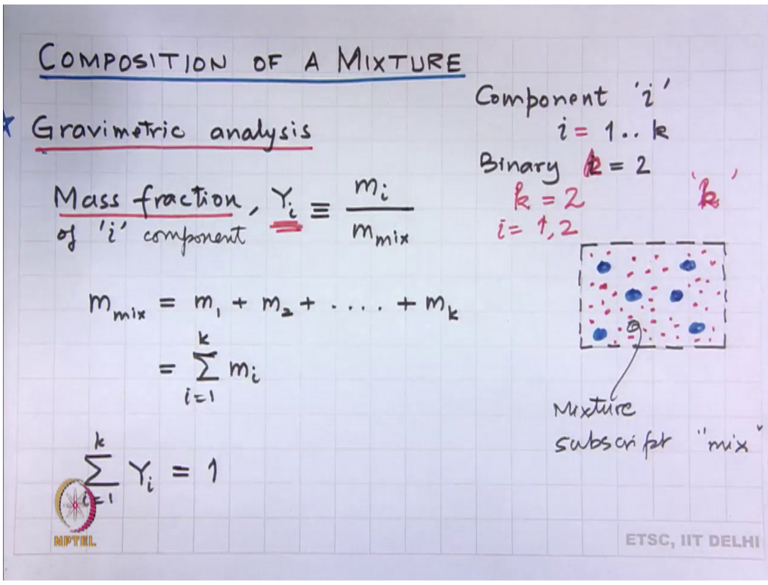

So, that question we are asking and so, the first person that we need to settle is how to quantify and specify exactly the composition of a mixture. There we have two options here, one is the gravimetric analysis and second which we look at is the molar analysis. So, what you are saying is we have a mixture of all these components, I am depicting here only two component mixture, but did not be the case and we will designate each component by i and the number of components in the mixture we will say is k. So, each component will be 1, 2, 3, 4 all the way till k. If it is a binary mixture we have k equal to 2 and so, the components will be i is equal to 1 or i is equal to 2.

So, that is what we have your depiction of a binary mixture. And now we ask we ask the first question that we will define now, what is mass fraction of the ith component. The symbol we will use is capital Y and we are looking at mass fraction of the ith components so subscript is i and this is mass of the ith component in the system divided by the mass of the mixture. So, we are doing an important thing here is to first say we define our system and whatever is contained in it this is our mixture; mixture and we will denote it in all our properties by the subscript mix m i x mixture.

So, there is some molecules of the first components, some of the second component and the mass fraction will be that in this system what is the mass of the ith component divided by the total mass of the mixture and that is the mass fraction of the ith component Y i.

So, mixture mass is nothing, but some of the mass of the individual components, m 1 plus m 2 plus all the way till m k what is the summation it is m i i equal to 1 to k and so, if we just we put these two together, we come up with a simple relation that summation of Y i is equal to 1. So, that is the sum of the mass fractions of individual components in a mixture is unity. So, this is one new thing we have added on which is our mass fraction and the symbol is Y i capital Y i.

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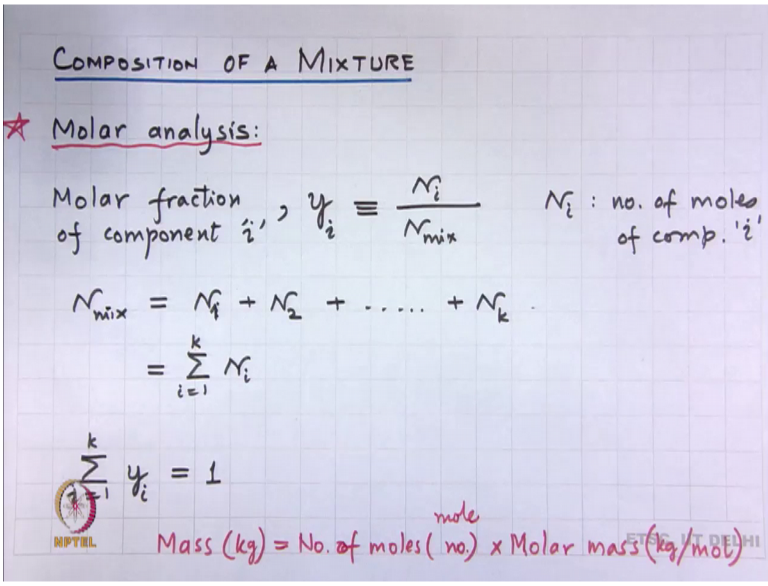

The second way to get the composition of a mixture is the molar analysis. And here instead of defining it as the ratio of masses we say that in that same system molar fraction of component i which is denoted now by a lowercase y small y i, as number of moles of the ith component divided by the number of moles in the mixture.

So, it is N i over n mix. The number of moles in the mixture is the sum of the number of moles of every individual component and that is summation N i, i equal to 1 to k. So, we again put this two together we get the summation of the molar fractions of each component in a mixture is 1 that is what this thing tells us.

Just to recap what we know from school chemistry days mass in kilograms is number of moles mole number multiplied by the molar mass, which is kilograms per mole are sometimes also referred to as the molecular weight. Now we will start combining those two and ask the question how do I get the mixture molar mass or the molecular weight of the mixture.

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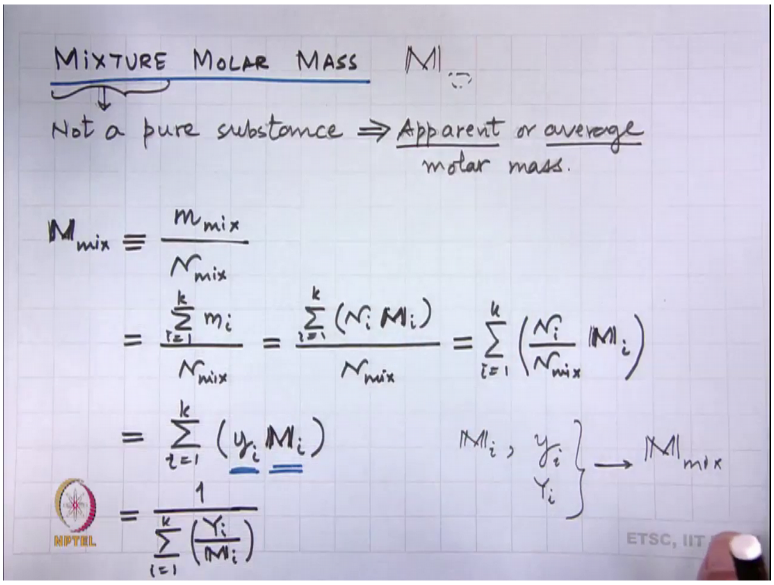

So, first thing to note is that the mixture is not a pure substance. So, when we talk of the molar mass of a mixture, it is some sort of a ambiguous term. So, we qualify that and say we will not call it the molar mass of the mixture, but prefix it with by saying that this is the apparent or the average molar mass of the mixture. And for molar mass we will use the symbol a darkened M and put the necessary subscripts depending on whose molar mass we are looking at.

So, molar mass of the mixture is mass of the mixture divided by the number of moles in the mixture, which is summation of the mass of the individual components divided by the total number of moles in the mixture and if we simplify it, we come with this thing that the summation of N i over N i N mix multiplied by the molar mass of the ith component M i which is nothing, but summation of molar fraction y i and the molar mass of the ith component. The product of this is summed up for all the components to give the mixture molar mass and in terms of the mass fraction, we can work this a little bit around.

This is one over submission from i equal to 1 to k mass fraction of ith component divided by molar mass of the ith component. So, which means what does this thing tell us is that, if in a mixture we know the molar masses of every component and the composition or the amount of each one of them y i or Y i in the mixture, then using these and this formula we can calculate and assign a number which is the apparent or average mixture molar mass, that is a new another new term that has now come about. Fortunately for a substance like air, oxygen and nitrogen are relatively similar type of molecules. So, the molar mixture molar mass of air is not drastically different from that of oxygen and nitrogen and the amount of errors we are likely to introduce this is not going to be very large, which is why we learnt in all the gas power cycles in that air standard cycle is a pretty good way to get a first and understanding of the system.

But if the mixture has very different molecules; say octane and oxygen or say hydrogen and nitrogen. Now we have very different molar masses and the apparent of average molar mass it will be at best be an approximate representation of what the mixture will do. Then the only option we have is to go to a further deeper analysis and not make this assumption that we are assigning a mixture of single molar mass. That is beyond the scope of this course.

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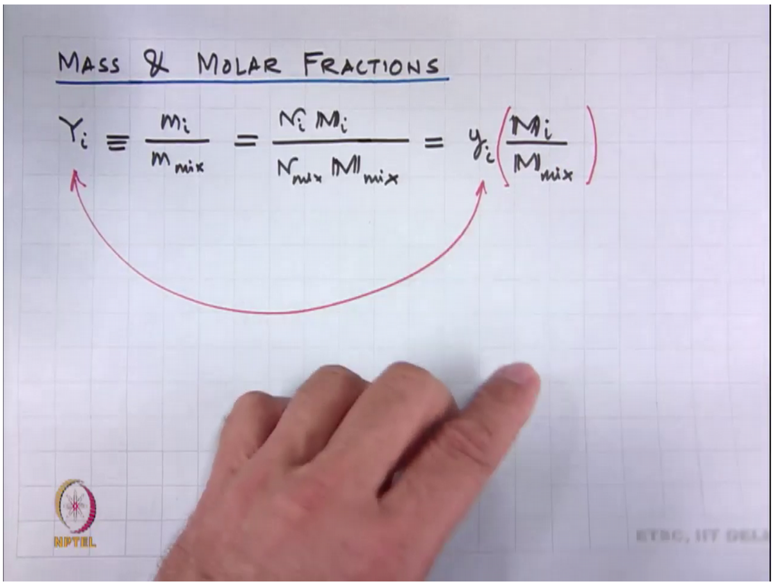

Now, we look at the relationship between mass and molar fractions. Mass fraction Y i is m i over a mixture and this is N i M i over N mix over M mix which is small y i into M i over n mix. So, this tells us a very simple thing here now that the small i and y i capital Y i they are connected by the ratio of the molar mass of the ith component and the mixture molar mass. So, we got one use of what we just defined as the mixture molar mass to correlate mass and molar fractions.

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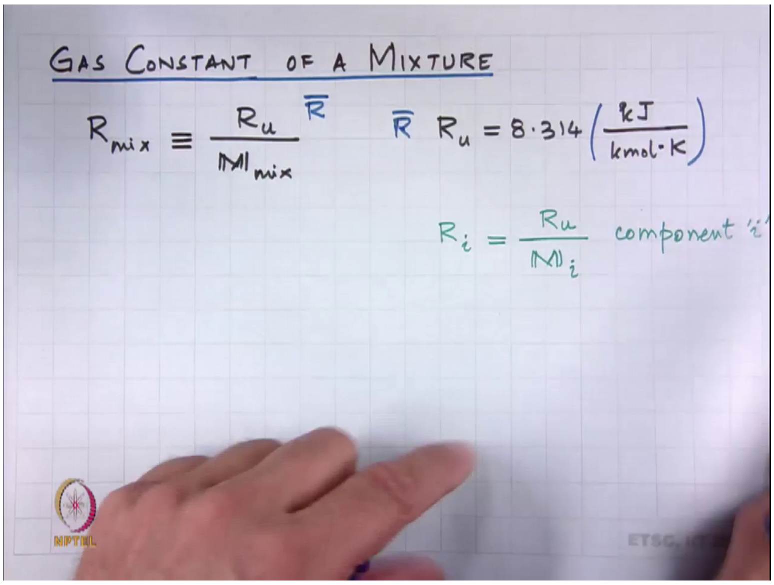

The next thing we would like to do that if we are looking at mixture of gases, then what is the gas constant? And we define it that the mixture gas constant is the universal gas constant which is R u or in some text you will see this as R bar divided by the mixture molar mass. The universal gas constant R u or R bar is 8.314 kilo Joules per kilo mole per Kelvin and what we have already done with the pure substance. For a pure substance the for ith component its gas constant is universal gas constant over its molar mass. So, this gives us yet another term which is the gas constant of the mixture.

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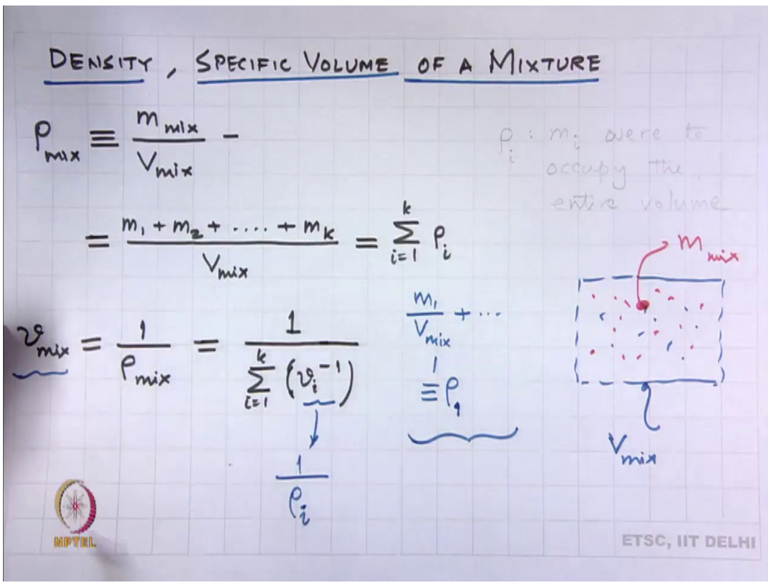

The next property we will look at density or the specific volume of a mixture. So, we define density of the mixture as the mass of the mixture divided by the volume of the mixture. That same system that we are drawn earlier this was a system whose volume is now V mix.

And the mass of all the components inside this is m mix and like the definition of density, the ratio of this is the density of the mixture the mixture mass we can write down in this way and if you open it up we can say that this is summation of rho i, i equal to 1 to k. So, what we have basically done is summed up m 1 over V mix plus like that for every other component. The important thing here is that this formula is applicable only when we say that the density of the mixture of the ith component is the density if it were to occupy the entire volume of the mixture all by itself.

That means if you remove all the other species from this volume, only the ith species remains there then that mass of the ith species mi or m 1 divided by the total volume with the mixture was occupying, this is defined as the rho 1. This is an important point to remember, it will come back again later on also. Then we can also do v mix with the specific volume of the mixture which is 1 upon rho mix which is equal to 1 upon summation v i to the power minus 1 and the same way we can work out that from the v i which is one upon rho i, we can sum up in this way to get the specific volume of the mixture.

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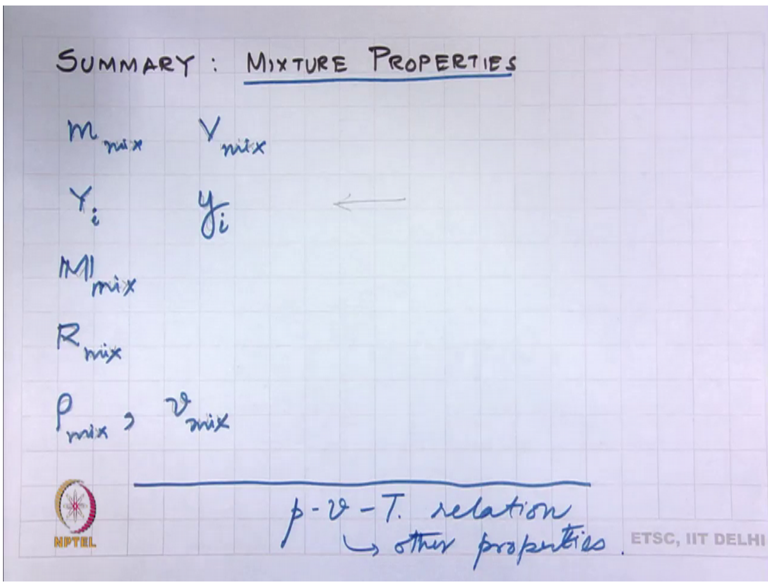

So, we will summarize this part of the lecture by saying that we have looked developed a whole bunch of basic properties of a mixture by defining what is the mass of the mixture, the volume of the mixture, the mass fraction is a new term we developed, the molar fraction mixture molar mass the gas constant of the mixture, density of the mixture and specific volume of the mixture.

So, we have developed the basic things that we required for the next part of the development, which is how it can be developed the p-v-T relation and get all the other properties which will complete our discussion of mixture properties. So, in the next lecture we will extend what we have learnt here to get the p-v-T relation and see how properties and property changes will happen. So, will conclude this module here.

Thank you.