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Properties of gas and vapour mixtures

Hello and welcome to lecture number 21 of this lecture series on introduction to aerospace propulsion.

We have been discussing over the last several lectures on basic aspects of thermodynamics, including some of the basic cycles which form very important aspects of engineering analysis and our day to day use as well. We have also had several tutorial sessions, during which we have solved some problems related to basic thermodynamics. In the last lecture, we have solved some problems related to cycle, analysis of some of the cycles like the Otto cycle, the diesel cycle, Eriksson cycle and the Brayton cycles.

What we shall be discussing today is a very different topic in some sense, as compared to what we have been discussing in the last few lectures. Of course, the discussions of today's lecture will also be an important aspect of thermodynamic analysis of certain systems which involve mixtures of gases or in processes which involve vapour. Water vapour for example, like if you have to use Rankine cycle for a steam power plant, how do you carry out a thermodynamic cycle analysis of such a cycle? Because Rankine cycle involves water and steam and therefore, we need to calculate properties associated with water and steam. So, today's lecture is aimed at understanding of properties of what are known as pure substances as well as mixture of ideal gases and real gases and so on.

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So what we shall be discussing in today's lecture are the following. We shall be talking about properties of pure substances, what are meant by pure substances. We shall then be discussing about what is meant by compressed liquid, saturated liquid, saturated vapour, superheated vapour and so on. We shall be also discussing about, what is meant by saturation temperature and pressure.

Then we shall be talking about property diagrams of pure substances, property tables, and composition of a gas mixture. Then we shall talk about P-v-T behavior of gas mixtures, ideal gas and real gas mixtures, and properties of gas mixtures. So, these are some of the aspects that we shall be discussing in today's lecture, which is primarily aimed at understanding of properties of pure substances.

What do we primarily mean by a pure substance? That is going to be our topic of discussion for today's lecture. Now, a pure substance is one which has a fixed composition throughout the process and such a substance is referred to as a pure substance. Examples of pure substances can be water or gases like nitrogen, oxygen, helium and so on. These are certain substance which will have the same composition throughout the process and that is why they are called pure substances.

A mixture of one or more phases of a pure substance will still remain to be pure substance, as long as the chemical composition of individual phases of the mixture does not change. That is a mixture of water and vapour; that is, water vapour will still be qualified as a pure substance because the chemical composition of neither water nor water vapour changes during the process. So as long as that is maintained, then even a mixture of different phases of the same substance which is a pure substance will still be called as pure substance in self. So, a substance which has a fixed chemical composition throughout is called a pure substance. Examples are water, nitrogen, helium and so on.

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A mixture of two or more phases of a pure substance will still be a pure substance, as long as the chemical composition of all the phases is the same mixture of ice in water and so on. Properties of water and its different phases form a very important part of analysis because in different engineering systems, one would come across use of water and its different phases like ice or steam. Therefore, analyzing different properties of water and its different phases will be a very significant part of an analysis of any system which involves water and its phases.

Therefore, it is important for us to understand the significance or importance of water and its different phases which are why we are basically trying to understand properties associated with water and its different phases. So, before we try and understand those properties, we need to understand certain terms associated with how water behaves at different states or phases. If we consider water which is at a state, which is far away from being vapourization that is water or a liquid which is at a state which is not about to vaporize is known as a compressed liquid or a subcooled liquid.

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So water or any other liquid when it exists in a state, therein it is not going to vaporize at all such a state of water or that liquid is called compressed liquid or subcooled liquid. For example, water at a temperature of 20 degree celsius and one atmosphere is a subcooled state because water is not at a state of evaporation at one atmosphere, because we all know that at one atmosphere water boils at 100 degree celsius.

A liquid that is about to vaporize is called a saturated liquid; that is a liquid which is in a state that it is just about to vaporize is known as a saturated liquid. A vapour on the other hand, which is about to condense is called saturated vapour.

So, vapour which has reached a state, wherein it is about to condense is known as saturated vapour and a vapour which is not about to condense, that is it is not a saturated vapour is called a superheated vapour. That is the vapour happens to be in a state, where even some amount of cooling does not cause it to condense is known as superheated vapour. When you have vapour which is at a temperature and pressure, which is not close to the saturation temperatures then, that vapour is known as superheated vapour.

So, what we have discussed are compressed liquid or subcooled liquid wherein the liquid is not about to vaporize. A liquid which is about to vaporize is called a saturated liquid, a vapour which is about to condense is called a saturated vapour and a vapour which is not about to condense is known as superheated vapour. What I will do now is to illustrate all these different states by some example. We will use water as our example because that is the most common liquid in that we come across in engineering systems.



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So, if you look at different states of water, let us look at state 1 for example. At state 1, water is at a pressure of one atmosphere and 20 degrees celsius, which means that the water is not about to vaporize, it is not at a state that it will begin to vaporize. Therefore, this particular state that is state 1 is known as the compressed liquid state for water.

Now we consider state 2; that is continuously as you can see, we are adding heat to the system as we add heat at constant pressure that is the pressure remaining constant now, the temperature increases. At the state 2, temperature of water is now 100 degree celsius pressure remains one atmosphere, so this state is known as saturated liquid state for water. That is water is at a state now that it would start vaporizing any minute now; that is at any moment, the water would start vaporizing which is why it is called saturated liquid.

State 3 is a mixture of saturated vapour and saturated liquid because as we continue to add heat at 100 degree celsius, water will start vaporizing provided pressure is one

atmosphere and once it start vaporizing you can see, there will be one part of the system which consists of a vapour of water and second part consists of saturated liquid. So, we have a mixture of saturated liquid vapour, so this is saturated liquid vapour mixture that is state 3.



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Looking at state 4, we again add heat continuously till a point where there is no more water left in the system. So at one atmosphere and 100 degree celsius if we have water vapour, then that is known as saturated vapour because if you start removing heat, water will or that is vapour will immediately begin to condense, so this is known as saturated vapour state.

State 5 is if we again add continuously heat at constant pressure that is one atmosphere then, we have higher temperature of the vapour which is not close to its condensation temperature. This is known as the superheated state of water or vapour, so state 5 is superheated vapour.

What we have seen are 5 different states of the same substance, the same pure substance that is water. State one was of water at a temperature and pressure which is far away from its vaporization temperature that is known as sub-cooled or compressed water state. Second state is if you heat water up to 100 degree celsius at one atmosphere, water is at a point that it may begin to vaporize any moment, so this is known as the saturated liquid state.

The third state is you again add heat water will begin to evapourate, so you will have a mixture of water and vapour at 100 degrees celsius and one atmosphere, so this is known as the saturated liquid or vapour mixture. Fourth state is that we have only vapour which is at 100 degrees celsius for water and so that state corresponds to saturated vapour state because the vapour will begin to condense at any moment.

The last state is at a temperature which is far away from the condensation temperature and that is known as the superheated vapour state, wherein the temperature is far away from the condensation temperature. So, for water temperatures much beyond 100 degrees celsius at one atmosphere would be superheated state of water.

So what we shall do now that we have 5 different states of water. Let us plot the temperature and volume, let us plot this particular process that we have seen of adding heat to water so has to get different states or phases of water and plot them on a constant pressure lines. So, what we have seen is in all the 5 different states that we have identified, pressure remains a constant that is one atmosphere.

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So on a constant pressure line, we will plot this property on temperature and specific volume coordinates. On T-v coordinates or T-v diagram temperature and specific volume, if you were to plot this particular process that we have seen which is basically from state 1 to state 5, this is a constant pressure process, it is constant pressure at pressure equal to 1 atmosphere. Water was initially at state 1 at 20 degrees celsius and as

you heat water at constant pressure, this is how the process proceeds up to state 2 (Refer Slide Time: 13:06). So, this is the compressed liquid state because at these states water is not in a position that it will begin to vaporize.

At state 2 is when you have saturated liquid that is 100 degree celsius, so water is in a position that it will begin to vaporize. State 2 corresponds to saturated liquid state. State 2 to state 3 is saturated mixture where you have liquid as well as the vapour and after it reaches state 3 and it goes to state 4, so any state in between 2 and 4 which is equal state 3 that is saturated mixture state.

After it reaches state 4, we have the saturated vapour state; that is we have only vapour which is saturated that is it may condense any moment. Further, addition of heat at constant pressure increases the temperature it was 100 from all the way from state 2 to state 4 and as we increase the temperature, we have process going from state 4 to state 5 and this is the super-heated state. That is we have now temperatures which are much higher than the condensation temperature.

The vapour reaches a temperature of 300 degrees celsius; let us say that was at state 5. So, state 5 is the superheated vapour state, so any point in the between 4 and 5 corresponds to superheated vapour. So, 4 5 is the superheated vapour state. This is how you would plot this process which is basically heating of water from subcooled state that is compressed liquid all the way up to superheated vapour state.

As you heat from state 1 to state 5, water passes through a series of different states which involves subcooled state, saturated liquid state, saturated liquid vapour mixture, saturated vapour and the superheated vapour. As we continuously heat at constant pressure, water passes through these different phases and we have discussed 5 different states of water which correspond to different states of water as well.

So, we can plot the property diagram on a constant pressure scale between temperature and specific volume and we can actually see the variation of the different properties of water as its passes through these different states. So, property basically the temperature in this case was changing but, the pressure was kept constant at one atmosphere.

It is also possible that you can change it the other way around that is we can also change pressure; that is as you keep changing pressures the characteristic curve that we have just seen will also change because this is valid only for pressure is equal to one atmosphere. For any other pressure, we know that the boiling point of water, the condensation point of vapour will all be different; which means that as you plot this for a different sets of pressure and temperatures, we should be able to get on T-v scale that is temperature volume scale, a series of these constant pressures lines along which water would continuously change its phase. This is what we shall try and do, and see different property diagrams or scales in which we can see how the properties of water would change.

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Now in order to do that, that is because temperature at which water would start boiling also depends upon pressure, it is a strong function of pressure and so if we fix pressure, the boiling temperature is also fixed. At a given pressure, the temperature at which a given pure substance changes its phase is called the saturation temperature or T sat as it is represented.

So once you fix the pressure, what is the temperature at which the phase changes that is basically known as the saturation temperature. Similarly, at a given temperature, the pressure at which a pure substance changes its phase is called the saturation pressure.

So saturation pressure and temperature are both functions of each other in some sense. That is if you fix the pressure, then the temperature at which a pure substance changes its phase is known as the saturation temperature and as you fix pressure, the temperature at which the property of the pure substance changes its phase is known as the saturation temperature. So, saturation pressure and temperature will form very important aspect of an analysis of the pure substances which continuously evolve and change their phase.

In the previous picture or diagram which I had shown, variation of the properties along a constant pressure line if you were to plot multiple number of these pressures what we get is a series of points. That is if you join all the state twos and state fours, we get saturation line on one side, we have a saturated liquid line on the other side, we have saturation vapour line and eventually this will meet at a particular point which is known as the critical temperature or critical point.

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So let us plot a series of these lines on T-v diagram, that is temperature and volume diagram. In the previous 2 slides from here, I had shown you a line which is looking this constant pressure line, compressed liquid, saturation liquid, mixture of saturation liquid and vapour, saturation vapour here and superheated vapour after this.

What if I plot this for multiple pressures? If I increase the pressure P 2 which is greater than P 1 but, is equal to a constant we get a line like this (Refer Slide Time: 19:19), that is for higher pressures, the temperatures will also now be different. As you increase the pressure, the boiling temperature of water also changes. You must have learnt in your school days earlier on that if you go to a high altitude place, water boils at a lower temperature; that is it boils at temperature lower than 100 degree celsius. At higher

altitudes, we know the pressure is lower and therefore, water will also boil at lower temperatures. That is if you were to plot below this, let us say this is atmospheric pressure one atmosphere, which is what we did last time and wherein water boils at 100 degree celsius. So, if you were plot this for let us say less than sub atmospheric pressure which will occur at high altitudes, water will boil at lower temperatures. Similarly, at higher pressures water boils at higher temperatures.

So you can see, if you plot multiple number of these pressure, constant pressure lines what we can see is and we join all these points locus of all these lines or points which joins state 2 which was the saturated liquid state of water, we get a saturated liquid line. On the other hand, if you join all states four which was saturated vapour state, we get a saturated vapour line and both these lines meet at a point which is known as the critical point.

All points on the left of the saturation line correspond to the compressed liquid state, all those points on the right hand side of the saturated vapour line corresponds to the superheated vapour state and those which fall within this curve corresponds to a mixture of saturated liquid and vapour.

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So this is basically a critical diagram which also shows how you can achieve a critical point when you were to plot different states of water for different pressures. In general, if I were to plot this for pressures which are higher than the critical pressure, which means that if you have a constant pressure process which has a pressure higher than let us say the critical point that is P greater than P critical. Then, what basically happens is at super critical pressures where pressure is greater than the critical pressure, there is no distinct phase change because phase change occurs only during the process which is below this curve (Refer Slide Time: 22:07); this is basically indicating the phase change process.



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So after the critical point, there is basically no distinct phase change process that takes place. At pressures which exceed the critical pressure, one cannot see a distinct phase change or a boiling process whereas, at pressures which are below the critical pressure there would be a very distinct phase change process or a boiling process during which liquid becomes vapour and so on.

There is a distinct phase change that occurs for processes which occur at pressures which are below the critical pressure. For pressures which are higher than the critical pressure there is no distinct phase change or boiling process that we can see during change of phase of a pure substance.

We have now plotted the phase change process in terms of temperature and specific volume coordinates where we have seen a constant pressure on a constant pressure line. How the different properties can change? How phase water changes its phase from or how water changes its state from subcooled state to saturated liquid state to mixture of saturated liquid and vapour then, saturated vapour and the superheated vapour.

So the locus of all the saturation lines which include the saturation liquid is known as the saturated liquid line. That is if you join all the state twos of a constant pressure lines we get saturated liquid line, if you join all the state four lines we get the saturated vapour line; eventually both these lines meet at a point which is known as the critical point. For pressures which exceed the critical pressure, one cannot really see a distinct phase change or boiling process.



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So, what we will do next is to plot phase change process on a P-T diagram; that is pressure and temperatures coordinates and see how the variation looks like. On pressure and temperature coordinates, if you were to plot the phase change process, so here we have the solid state, the liquid state and the vapour state. If you were to look at a process, were the pressure and temperatures are changing for pressures and temperatures below the triple point.

Triple point is by definition the point at which all the 3 phases coexist in equilibrium that is solid, liquid and vapour and for water the triple point is 0.01 degrees celsius. So, a line which basically demarcates the solid from the vapour that is at pressures which are lower than what corresponds to the triple point or temperature as well as pressure, the process which will occur would basically be a sublimation process. That is solid would directly become a vapour without becoming a liquid, that is if we have pressures and temperature which are below that of the triple point then, if you take up ice for example, ice will directly vaporize into water vapour without actually melting.

Melting would occur only at temperatures and pressures which correspond to what is shown here (Refer Slide Time: 25:40). There are 2 melting lines shown, there are substances that expand on freezing and there are substances that contract on freezing. For example, water is a substance which expands on freezing and so the melting line for water is which is basically has a negative slope, whereas those substances which contract on freezing have a positive slope of this melting line.

So, water will follow this melting line because its temperature and pressure is above the critical point or above the triple point. Solid ice would melt and become liquid, as we have seen this is basically the vapourization line where on further addition of heat, water would become vapour. You also have the critical points shown here. So, critical point was also defined in the previous diagram here and this is of course on temperature and volume coordinates, this is on pressure and temperature coordinates.

This is basically a pressure temperature diagram of any pure substance and the difference between different pure substances will come in the location of the triple point as well as the critical point because that is different for different pure substances. For example, for water the melting line is slightly different from the melting line for substances that contract on freezing and so on. There are 3 distinct phases that you can see here: the solid phase which is between the sublimation line and the melting line, the liquid phase is between the melting line and vapourization line and the vapour phase is between the sublimation line and the vapourization line. The point at which all these three phases coexist is known as the triple point.

We have plotted the properties on different scales on temperature volume, pressure temperature and so on and it is also possible to plot these diagrams on a three dimensional plot which is known as the PVT surface. Pressure Volume Temperature surface, which is basically a combination of pressure volume, pressure temperature and temperature volume coordinates and so on.

Now, the properties of different substances of pure substances are either plotted in terms of these coordinates or you can also see them in terms of a tabular format or there are tables associated with properties of pure substances. Because the thermodynamic relation for different substances can be quite complicated and so calculating each of the properties like enthalpy, entropy etcetera at different pressures and temperatures can be quite involved. To avoid that there are standard property tables available where in for given pressure and temperature one can determine the different properties like energy, the entropy and enthalpy and also specific volume of different pure substances.

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If you look at the property table which is something we shall be discussing now, basically the properties are in the form of tables. So, there are different properties tables available for different substances and properties of water are usually refer to as the steam table where we get different properties of water, liquid, water vapour as well as superheated steam.

In all these tables subscript f is used for denoting properties of saturated liquid and subscript g denotes properties of saturated vapour. Also, f g denotes the difference between saturated vapour and saturated liquid values of the same property.

So, in these tables you would find subscript f which corresponds to properties of liquids that is saturated liquid; subscript g denotes properties of saturated vapour and subscript f g denotes the difference between these two of the same properties.

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For example, h f that is h subscript f basically corresponds to specific enthalpy of the saturated liquid, h subscript g is the specific enthalpy of the saturated vapour. Therefore, h f g is the difference between h g and h f that is h f g is equal to h g minus h f; that is basically the difference between specific enthalpy of the saturated vapour and specific enthalpy of the saturated liquid.

If you recall in the property diagram, I have shown that process from 2 to 4 corresponds to the phase change process. Therefore, the difference between enthalpies of the vapour

and that of the saturated liquid is basically the enthalpy of vapourization or latent heat of vapourization. That is the difference h g and h f is the difference between the specific enthalpy of the saturated vapour and specific enthalpy of the saturated liquid which means, the difference between the 2 basically corresponds to the amount of energy required for carrying out this phase change from liquid to vapour. Therefore, h f g is basically the latent heat of vapourization or enthalpy of vapourization as it is also sometimes called.

Now, within this saturation curve that we have drawn where we have a mixture of saturation liquid as well as vapour, we know that there is some fraction of liquid water present; there is some fraction of vapour present. So, we will now represent this fraction by what is known as quality. That is what is the quality associated with this particular vapour and liquid mixture.

So, quality which is usually denoted by symbol x. Quality x is basically the ratio of mass of water mass of what vapour to the mass of liquid; that is quality x is basically the ratio of mass of the vapour present to the mass of liquid present.

Therefore, quality has a value which ranges from 0 to 1 which means, if quality has a value of 0 it means that the mass of vapour present is 0 and so the entire mass is basically the mass of liquid. So, its quality of 0 corresponds to saturated liquid state and quality of 1 corresponds to saturated vapour state because it is at that state where the entire mass corresponds to the mass of the vapour itself. So, any value of quality which is between 0 and 1 corresponds to a mixture of saturated liquid and vapour state.

So quality x is basically defined as ratio of the mass of the vapour to the mass of liquid and it has a value obviously ranging from 0 to 1.

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So x equal to 0 means a saturated liquid state, x is equal to 1 means a saturated vapour state. Now, we can actually show that in general any property which is denoted by y, y average should be equal to the sum of y f plus x times y fg; that is sum of the property of the saturated liquid plus quality multiplied by the difference in the property at saturated vapour and saturated liquid state.

So here y can take any value, it could be either specific volume or it could be energy, specific entropy or specific enthalpy. For example, we can write h average is equal to h f which is the enthalpy corresponding to the saturated liquid state plus the x which is basically the quality multiplied by h fg which is h g minus h f. So, most of the times, we would drop this subscript average because it is known that we just taking an average of the property. It is basically h is equal to h f plus x times h fg.

Similarly, we can write u is equal u f plus x times u fg, s is equal to s f is equal to x times s x fg and so on. It is also known that the value or the property at liquid state - that is h f or u f or s f should be less than or equal to the average value which will in turn be less than or equal to the value at the vapour state because, at the vapour state it also as additional energy because of the latent heat.

So y f will be less than or equal to y average, less than or equal to y g and so this is true for any of these properties, whether it is specific volume or specific internal energy or entropy or enthalpy and so on. So what we have seen is that from a property table if you look at properties of steam for a particular pressure and temperature, all these properties will be listed as different columns. You would have h f h fg and h g similarly, you would in properties for internal energy, entropy and specific volume. So from the table its possible for us to determine these values rather than calculate them though it is possible to calculate them but, it can be quite complicated especially if you look at mixture of liquid and mixtures and so on.

So to keep things simple, especially when you are trying to solve problems, property tables come in handy because based on the pressure and temperature one can determine all these properties corresponding to that particular pressure and temperature.

INTRODUCTION TO AEROSPACE PROPULSION Lect-21 Properties of pure substances Critical Т point P2=const. >P1 Compressed 3 liquid Superheated vapour P₁=const. Saturated liquid line Saturated vapour line Saturated liquid- vapour v T-v diagram of a pure substance

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Now we have seen that, on pressure temperature diagrams as well as, we have also shown the temperature and volume diagram. Let us look at the temperature and volume diagram of a pure substance again.

Here, we can see that on the left hand side of the saturated liquid line, it is the compressed liquid state and on the right hand side of the saturated vapour line is the superheated vapour state. So, let us look at some more properties of the superheated vapour state. All those properties which correspond to the right hand side of this vapour line, saturated vapour line correspond to superheated vapour.

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Region to the right of the vapour line and at temperatures above the critical temperature we have the superheated vapour region. In the superheated region which is basically a single phase region, pressure and temperature are no longer dependent properties. That is you can change pressure and temperature independent of each other, unlike at other phases where they are basically dependent.

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So compared to a saturated vapour, a superheated vapour is characterized by the following. That is if you compare superheated vapour and a saturated vapour,

superheated vapour is characterized by lower pressures; that is P will be less than saturated pressure for a given temperature. Temperature would be greater than saturated temperatures at a given pressure that is if you look at the pressures and temperature for a given temperature, pressure will be higher than that of the saturation pressure and if you look at the same pressure, the temperature will be higher than that of the saturation temperature for superheated state.

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Also in superheated state, the specific volume enthalpy etcetera are higher than that at a given pressure or temperature. That is for superheated steam for example, volume would be higher than that of the volume of the saturated vapour. Similarly, enthalpy of the superheated vapour will be greater than the enthalpy of the saturated vapour, internal energy of the superheated vapour is greater than enthalpy of saturated vapour for a given pressure or temperature.

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So these are some of the properties that are associated with superheated vapour. Similarly, we can also identify properties that are correspond to that of subcooled liquid which will be basically those points which are on the left hand side of the saturated liquid line; so that though all those points correspond to the compressed liquid state of the particular pure substance.

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Now what we shall discuss next is on composition of a gas mixture. That is if you were to look at a mixture of different gases, how do you analyze different properties of that particular mixture and if you have to calculate enthalpy of the mixture, how do you calculate them? In order to do that, we will define what are known as mass fractions and mole fractions of a particular mixture and then apply those for calculating different properties.

So let us consider a gas mixture which has let us say k components and let m subscript m be the mass of the mixture and N subscript m is the number of moles. Therefore, m subscript m is equal to summation i is equal to 1 to k m i and N m is equal to summation i is equal to 1 to k N i. Here, let us also define mass fraction m f which is ratio of the mass of a component to the mass of the mixture. Mole fraction y is basically the ratio of the mole number of a component to the mole number of the mixture.

So m f i is equal to m i by m m that is mass of the component divided by mass of the mixture and mole fraction is mole number of the component to the mole number of the mixture.

So, mass of a substance of N and molar mass that of M will basically be equal to product of the two, that is mole number multiplied by the molar mass. The average molar mass and gas constant can also be calculated as M subscript m is equal to the mass of the mixture divided by the molar number of that particular mixture which is basically equal to sigma m i divided by N m which is sigma N i M i divided by N m. Since N i by N m is equal to the mole fraction, this is equal to sigma summation i is equal to 1 to k, y i M i. Therefore, the average gas constant for the mixture would be equal to universal gas constant divided by average molar mass of that particular mixture.

So which means that, we can also now relate mass and mole fractions of the mixture using this mass fraction, which is m f i is equal to m i divided by the mass of the mixture which is finally, equal to the mole fraction y i multiplied by M i by M m. The mass and mole fractions are basically related through the mass fraction m f i is equal to the mole fraction multiplied by the molar mass m i by m m.

This is basically to calculate, if you were to calculate different properties of a gas mixture, you can basically use some of these properties to identify and calculate average properties of a mixture of gases like average gas constant and so on. We shall also see how you can calculate average properties in terms of enthalpies and specific heats and so on. We have also already discussed in two three lectures earlier, about ideal gas equation and compressibility factor.

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Ideal gas equation with a compressibility factor can be used for real gases; this is something we have discussed earlier. So, prediction of the behavior of gas mixtures can basically be whether it is real gas or ideal gas can be predicted by based on two laws. One is known as the Dalton's law of additive pressures and the other is known as Amagat's law of additive volumes.

So, Dalton's law of additive pressure probably you would have learnt this earlier is basically stating that, the pressure of a gas mixture is equal to the sum of the pressures of each gas that if it would exert if it existed alone at the mixture of volume and temperature.

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Similarly, the Amagat's law of additive volume states that, volume of a gas mixture is equal to the sum of the volumes each gas would occupy if it existed alone at the mixture temperature and pressure.

Both these laws can be used as it is for ideal gases but, these are kind of approximations for real gases that is, these laws can be used in an approximate way for real gases; one of the ways we could do that is by using the compressibility factor as well. Now, for ideal gases both these laws that is, whether it is Dalton's law or the Amagat's law, both of them give identical results whereas, it could give different results for real gases. Let us look at the Amagat's law and the Dalton's law.

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Dalton's law basically states that the mixture pressure is equal to summation i is equal to 1 to k, P i which is the component pressure at the temperature and volume of the mixture. Amagat's law states that V m - volume of the mixture is equal to summation i is equal to 1 to k V i at the mixture temperature and volume. So, both these equations are exact for ideal gases but, obviously they are only approximate for real gases.

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So for ideal gases, the component pressures and volume can be related to the mole fraction from the ideal gas equation that is P i we will use ideal gas equation for this P i;

that is component pressure at the temperature and volume T m V m divided by mixture pressure is equal to N i R u T m by V m, which is for the component divided by N m R u T m by V m which is for the mixture.

So, this reduces to N i by N m that is why that is the mole fraction. Similarly, we can also using the Amagat's law and we can still write or equate that being equal to the mole fraction that is the ratio of the component pressure to the mixture pressure and component volume to the mixture volume is basically the mole fraction. That is P i by P m is equal to V i by V m which is equal to number of moles ratio which is basically the mole fraction.

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So this quantity which is product of y i times P m is called the partial pressure and the product y i by y i times the mixture volume is called the partial volume. For an ideal gas mixture all these that is the mole fraction, the pressure fraction, and the volume fraction all of them are identical which is what I had mentioned here. For an ideal gas this pressure ratio, the pressure fraction, the volume fraction and mole fraction they are all basically the same but, they are not necessarily the same for real gases because if you were to see a real gas because of real gas effects all these parameters need not necessarily be the same.

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Let us look at real gases and how we apply Dalton's and Amagat's law for real gases. What we could either do is use one of the advanced equations of states like van der waals' equation or the Beattie-Bridgeman equation or so on or we could use the ideal gas equation itself with the compressibility factor.

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Dalton's law and Amagat's law can be use for real gases with approximations. So either we use advanced equations which can be little complicated or we use the compressibility factor where PV is equal to ZNR u T, where z is the compressibility factor.

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So Z compressibility factor for the mixture can be calculated if we know the compressibility factor for individual components. Z m is equal to summation i is equal to 1 to k y i Z i where, y i is the mole fraction for each of the components. So, Z i can be determined the either at T m and V m which based on Dalton's law or at T m and P m which is based on the Amagat's law for individual gases.

Again because these are not ideal gases, if you determine either of these ways they are not going to give you the same results but, what has been seen is that the Dalton's law seems to give more accurate results, if you were to determine the compressibility factor at the mixture temperature and mixture volume.

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So for gas mixtures, if you were required to calculate extensive properties like energy, enthalpy, and entropy and so on, how do you calculate that? We can calculate them if we know the contribution of each of the individual components. For example, the internal energy, enthalpy, entropy can be expressed as of the mixture U m energy of the mixture is equal to summation i is equal to 1 to k U i which is equal to summation i is equal to 1 k, m i u i where, m i is the mass of individual component, u i is the energy associated with the individual component.

Similarly, enthalpy and entropy can be expressed as summation of the products of the mass times the specific enthalpies and specific entropies of the individual components.

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Now, internal energy, enthalpy, entropy per unit mass can be basically determined by dividing the equations by the mass of the mixture. That is u m that is specific internal energy of the mixture will be equal to summation i is equal to 1 to k.

Mass fraction multiplied by the internal energy for each of the component similarly, enthalpy of the mixture will be equal to summation i equal to 1 to k mass fraction multiplied by enthalpy of individual components. For entropy of the mixture will be equal to summation i is equal to 1 to k, m f i times s i where, m f i is the mass fraction, s i corresponds to entropy of individual components.

We can also use similar properties for calculating the specific heat at constant volume and specific heat at constant pressure for the mixture; that is c v m specific heat at constant volume for the mixture will be equal to summation i is equal to 1 to k m f i times c v i where, c v i is the specific heat at constant volume for individual components. Similarly, c p m that is specific heat constant pressure for the mixture will be equal to summation i is equal to 1 to k m f i times c p i.

For gas mixtures, if you were to look at a mixture comprising of several gas components we can calculate the specific heats, we can calculate the internal energy, enthalpy, entropy etcetera for the mixture by summation of the mass fractions times the specific properties of the individual components. That is mass fraction multiplied by let us say enthalpy of one component and sum it up for all of these individual components, we get the specific enthalpy of the whole mixture.

We can also use the same properties for calculating the specific heats at constant pressure and constant volume for the mixture. Now, if you look at changes in these properties that are changes in enthalpy, changes in internal energy and entropy, we use the same principle that we have used for calculating the entropy, enthalpy, and internal energy of the mixture itself.

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So for calculating changes in the internal energy, enthalpy and entropy of a gas mixture during a process, we can calculate them as in the following way. Delta U m which is the change in energy of the mixture is equal to the sigma that is summation i is equal to 1 to k delta U i which is equal to summation i equal to 1 to k m i delta u i. Similarly, delta H m is equal to summation i is equal to 1 to k m i delta h i and for entropy delta S m is equal to summation i equal to 1 to k m i delta s i.

So that brings us to the end of this lecture, where we have been discussing about properties of pure substances.

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We have defined what is pure a substance, we have also defined what is meant by compressed liquid, saturated liquid, saturated vapour and superheated vapour. Basically, these are different states of water as they change phase from liquid to vapour. We have defined what is meant by saturation temperature and pressure; we have discussed different ways of expressing these phase change processes in terms of property diagrams of pure substances, p-v and p-t diagrams and temperature volume diagrams.

Property tables are those which basically help us in estimating many of these properties that is temperature and enthalpy, energy and so on. If we know the pressure and temperature of a particular process then we have also looked at pressure P-v-T behavior of gas mixtures and ideal gas and real gas mixtures and properties associated with gas mixtures on how you can calculate the different properties like enthalpy, entropy and internal energy of a gas mixture, if we know the mass friction of each of the components and the corresponding specific properties of that particular component. These are the topics we had discussed during this particular lecture.

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In the next lecture, what we shall be discussing are certain aspects which are quite different from what we have been discussing so far. We shall talk about one dimensional compressible flow and we shall define what are known as stagnation properties and then we will define Mach number and the speed of sound and we shall take up analysis of one dimensional isentropic flow.

We shall understand the variation of fluid velocity with flow area and also look at isentropic flow through nozzles; that is convergent nozzles as well as converging and diverging nozzles. So, isentropic flow through these different types of nozzles is something we shall be discussing in next lecture, as well as one dimensional flow compressible flow and properties of compressible flows is something that we shall be discussing in the next lecture, which we will be lecture number 22.