Engineering Thermodynamics

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Week-12
Lecture-52
Gas Mixture

Welcome to the new lecture on gas mixtures and non-reactive gas mixtures. We have just studied thermodynamic relations and properties. A non-reactive gas mixture is a simple mixing of two gases which do not react. In such cases, we can make tables of the properties of tea. For example, we have air. Different gases are mixed in the air, but they don't react. So, there are tables of air. But if you want, you can make more of these mixed gases. But the problem is how many tables you will make. So, some rules have been taken out. And this will be discussed. This is the lecture on this. In this video, we will understand the rules of non-reactive gas mixture which we can use the properties of mixture composition and individual component to get the properties of mixture So we will understand how you define composition of mixture like in mass fraction, mole fraction, volume fraction and how you apply the rules we have made in the ideal gas mixture and real gas mixture We will also discuss about the Dalton’s law and Market’s law which you must have read before and finally we will do an energy or energy analysis of a mixing process. So, let's start with the composition of gas mixture which we know that in general we define in two forms. We will either do the composition in the form of molar analysis which is the basis of molar or mass basis which we call gravimetric analysis. In the gravity analysis, you specify mass, and, in the molar, you specify the number of moles. We can do two types of analysis. And this will be to tell the composition of any mixture. It will be to tell whether the composition was based on the molar or the mass. So, mass means gravimetric analysis. And if you are talking about composition, let's say that you have a mixture of hydrogen and oxygen. Hydrogen is 6 kg and oxygen are 32 kg. What is the mass of the mixture? Because it is non-reactive, we simply add that it is 38 kg. Because 32 plus 6 is 38 kg. So, the mass of the mixture, which we call mm, is the sum of the individual mass of the component. Isn't it? And if we talk about moles, then here also there are 3 Kmol's and this is 1 Kmol, this is the mixture we are talking about So in this, what is the definition of moles? The mole is the mass, which is divided by molecular weight, so this is 6 by 2 So this is N of H2 6 by 2 is your molecular weight, so this is 3 kilomole. And this is 32 by 32, so this is 1 kilomole. So, if you add both, it is 4 kilomoles. So, you can also sum this. Like the moles of the mixture is the sum of individual component moles.

Now let's talk about how much mass fraction is there in the hydrogen mixture. So, what will you get? Mfi. I mean component, mass fraction of i. i mean component, so MF of hydrogen. So, this is mass of I divided by mass of the mixture. So, if we talk about H2, what will come out? Mass of the hydrogen is 6 divided by mass of the mixture is 38. So, this will come out. number of moles of component i divided by number of moles of the mixture so here if we talk about y of s2 so this will be your moles of s2, n of s2 divided by n of mixture so this is 3 kilo mole divided by 4 kilo mole so this is your 3 by 4 Mole fraction is represented in the form of y and mass fraction is represented as mf. Let's move forward and try to understand this. One thing is clear, since it is a fraction, when you sum the components in the fraction, then it should be 1. So, the sum of mass and mole fraction of a mixture, whether it is mass fraction or mole fraction, will always be 1. Like in this case, what we called as H2 plus O2, so ys2 was 3 by 4, so it is around 0.75 So y of O2 is 0.25, so this is also 1 So sum of molar fraction for mixture is equal to 1 let's write this in its form If we talk about molar mass So it also has expressions in simpler form Let's discuss about it

Apparent molar mass

$$M_m = \frac{m_m}{N_m} = \frac{\sum m_i}{N_m} = \frac{\sum N_i m_i}{N_m} = \sum_{i=1}^{k} y_i M_i$$

$$m = NM; \sum_{i=1}^{k} mf_i = 1 \; and \; \sum_{i=1}^{k} y_i = 1$$

$$gas\ constant\ R_m = \frac{R_u}{M_m}$$

The molar mass of mixture can be expressed,

$$M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum \frac{m_i}{(m_m M_i)}} = \frac{1}{\sum_{i=1}^{k} \frac{mf_i}{M_i}}$$

$$mf_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m}$$

This is derived from this. So molar mass of mixture is sum of mole fraction multiplied by molecular weight of molar mass of individual component. So, if you multiply molar mass of individual component by mole fraction and then sum every component, then you will get molar mass of the mixture. Similarly, you can also calculate the gas constant, i.e. Rm divided by Mi, which is the basic definition. Since this is a simple definition, we will use it later on, it depends on the problem statement. But in general, if we divide the universal gas constant, then you will get the gas constant for the mixture. So, similarly, we talked about molar mass. We can also represent this in another way. The first method was done in mole fraction. If you are asked to do the same thing in mass fraction, how will you do it? So, by definition, the mixture of mole and mass is M of M, i.e. mass of the mixture divided by moles of the mixture. So, we can change the moles of the mixture. We can write this as Mi divided by mole and mass of individual component. And this term is Mi. We can write mi, we can simplify this more. We can write to mi, now this is constant. We can write mi and we can bring it down. So, this will come out in this form. And we can represent mi by m, which is here. If we see from here, this is your m of i. Because mi by m is m of i. m of i divided by mi. So, this expression is capital M. 1 by summation mfi divided by mi, i equal to 1 to k. So, we can write molar mass fraction and mass fraction in this way, both expressions come out like this. We have written this part as well, there is a relation between these two. mfi is mi by ma. We can write this as this. And we can write this as this. and this part is your yi, so yi multiplied by mi by mb so it can be written like this so this is a basic mathematical way of expression some people must have read this type of expression before now let's talk about PVT behavior of gas mixture so for this, since this is a non-reactive mixture, we will understand two models one is Dalton's law of additive pressure In which we understand that the pressure of the gas mixture is equal to the pressure of the whole mixture. You will sum it up. You will keep summing the pressure that each gas is contributing. We will assume it as such that the molecules of the individual component are occupied by the volume and temperature. You will take out the pressure and then you will keep on summing it. So, this is the Doulton's law of additive pressure. Additive pressure means, suppose for example, your component, it has A and B, its volume is V and T, so A and B are both gas components, so you will take out this V and T and you will assume that this A is full, Let's say the pressure is Pa and we add this to V and T and the pressure is Pv. So what is the total pressure? P is equal to Pa plus Pv. So this is what Dalton's law of additive pressure says. would occupy if it exists alone at the mixture temperature pressure. What is said in this? The law of additive volume says that suppose you have temperature pressure. Now, according to the pressure, because here the volume is fixed, in this case the volume was fixed, here it is not necessary that the volume is fixed, you took the system, suppose A plus B, okay? We are saying that volume V is VA plus VB. And how will we get VA? We will assume that the temperature pressure is given. According to this, volume V is this. If you assume that this is the temperature pressure and if this gas exists separately, then the volume that comes out of this temperature pressure is VB. And then you add both VA and VB. So, we will call this Emigrants law of additive. So, this is what we are showing here. So, this is Dalton's law of additive pressure. It is in two ideal gas conditions. That's why it is an ideal gas relation. Because it is non-reactive here and it is acting like an ideal gas. And Amagat's law of additive volume for mixture of two ideal gases. Here, a simple volume addition is done. At any pressure or temperature. At the pressure of the volume. And likewise, what is Amagat's law? Vm summation Vi. Which is the individual volume of the temperature mixture and pressure mixture. So this is... It is exact for the ideal gas, and we are approximating it for the real gas. Now, the special thing is that Pi is the pressure of the component and vi is the volume of the component. And P by PM is the pressure fraction and V by Vm is the volume fraction. Now, you understand this. This is oxygen and nitrogen. These are the conditions of the mixture. 100 kPa, 400 K, 1 m3. So, you can see this because it is different. The volume of the component is 0.3. If you see the oxygen level in this condition, it will occupy 0.3 volume at 400 kPa. And this one will occupy 0.7 m3. These two will be added later. You can also think of it as if this is the ideal gas, then this is also partial volume which is mole Vi times multiplied by Vm. So if Vm is 1 meter cube in total, according to Vi or mole fractions, this oxygen will be 0.3, and nitrogen will be 0.7, if you consider it as 30% or 70%. So we can also extract component volume in this way. We can also extract the volume fraction in a simple way for the ideal glass. We will discuss this further and try to understand it through some questions. As I said, the fraction of Pi is not 1 because it is a mixture. It is connected through different compartments. But what happens if we can extract it? Ni, Ru, Tm, Vm are talking about the ideal gas. If the mixture is ideal gas, then all the components in the mixture are forming towards ideal gas So if the mixture is PM, then what will be the ideal gas of the mixture? PM, Vm, Nm, Ru, Tm. So, this is the total volume. Similarly, Pi is Ni, Ru, Tm, Vm. Tm, the temperature of the mixture, will be Vm. So, this is your Dalton's law. So, if you notice, if you take the ratio Pi by Pm, then this is your first term, this is the second term, this is the third term. So, this gets cancelled. The rest will be cancelled. What will remain is Ni by NiM, which is Yi. Similarly, According to Amagat's law, if we take Vi by Vm, then we write it as, because the pressure is fixed. So, Ni Ru Tm is the numerator, which is Vi by Pm. And denominator is of mixture. Nm Ru Tm divided by Pm. It comes from here. But according to Amagat's law, we are taking volume fraction. So, volume fraction also comes from mole fraction. Pi by Pm or Vi by Vm are the mole fraction. This is valid for the ideal gas mixture. If we carefully write down the yi, we can write Pi as yi Pm and also write vi as yi Vm. This term is called partial pressure. P i is called partial pressure. It is identical to the component pressure of the ideal gas. It is identical to the same, if you keep the individual component at the same volume or temperature, then only this much pressure will come, but whatever it contributes to the mixture, it is called partial pressure. And in the same way, if we take temperature and pressure, then your Amagat's law law says that the volume fraction is y i, which means y i V m is partial volume. So this VI is called partial volume. Sometimes, if we want to analyze the gas mixture, we take out the composition. And sometimes, the composition is taken out according to the volumetric analysis. The composition of the ideal gas mixture. This is an example of burning and combustion chambers. We will read the following questions. Orsat analysis is the composition of the ideal gas mixture. And it is done using the composition chamber. But it is based on volumetric analysis. And we will talk about it later. But normally Orsat analysis is quite common. In this, what we have understood now, partial pressure, volume, all this will come in handy. So, as we were talking about the ideal gas, the same way, the real gas also has Dalton’s law of additive pressure, Amherst's law of additive volume, this is useful. But, the component pressure, component volume, since the real gas will deviate from your ideal gas behavior, so, we will have to account for its deviation somewhere. Meaning, we will have to use it somewhere. For such deviation, we have 3 options. Either you take the exact table in any form, or you have the equation of state, or you have a compressive factor like pv is equal to z. z will be 1 because it is a vital gas, otherwise it will be greater than 1. So, in such cases you have to use it. If you have a mixer, you will get yizi, which is the mole fraction multiplied by zi, which is the compressibility factor of different components in TM and VM. You can calculate the deviation of the ideal gas using these three options. This concept can be applied to real gas as well. Remember that the simple equation of state can be written in this form in which Zm is the compressibility factor and this is the summation of Yi Zi in which Zi is the compressibility factor of the individual component. So Zi is applied to Tm and Vm if we apply according to Dalton’s law in which Tm and Vm are given. or according to Amagat's law, if Tm and Pm are given, then we will take out Zi on Tm and Pm. Dalton's law usually gives better and more accurate results than Amagat's law. So, pressure additive is more correct than volume additive. Let's move ahead and try to understand it. The second method is that you can use the pseudo-critical concept. ZM is determined by the pseudo-critical property. Pseudo-critical means that you are doing that it has its own tables and rules. critical pressure and critical temperature but pseudo means you are doing it with approximation in this you do pressure critical yi mole fraction multiplied by critical pressure component i so you have taken weighted average of each component in the same way you take out T critical summation yi Tcr so after taking out both normally when you Compressibility chart is used, so you use TR So when you are using Tr, you take T divided by TC So if it is a mixture, then this mixture is a simple critical mixture So this is Tm divided by Tcr So here in this way, Prm Pm divided by Tpcr m We are using this dash If you are using a mixer, then take the weighted average And from here, you can get effective Reduce temperature and pressure You can get effective reduced temperature and pressure Then you can get the compressibility chart That will be on Tr Pr And from here, you can get the compressibility chart ZM And if you get ZM, then you can get the rest So, in this kind of methods, we will use case rules, which is this. Okay? And normally, case rules give 10% broader result. So, in a way, it gives decent result, very valuable result. I mean, it is not so accurate, but 10% within the range. So, this is an acceptable result for engineering applications. Let's move ahead. Now, we will talk about other properties like enthalpy, internal energy, entropy We have seen that we have used weight traction because they were intensive properties In this case, normally when the pressure was intense, then these were all intensive properties but when the volume was high, then we added volume directly But for the rest of the properties, we will use it as simple as possible. We will add the properties of the individual components according to the extensive properties. We will use it as we have used it for volume. We will use the sum of the Intel Energy for individual components of the mixture.

$$U_m = \sum_{i=1}^{k} U_i = \sum_{i=1}^{k} m_i u_i = \sum_{i=1}^{k} N_i \bar{u}_i$$

$$H_m = \sum_{i=1}^{k} H_i = \sum_{i=1}^{k} m_i h_i = \sum_{i=1}^{k} N_i \bar{h}_i$$

$$S_m = \sum_{i=1}^{k} S_i = \sum_{i=1}^{k} m_i s_i = \sum_{i=1}^{k} N_i \bar{s}_i$$

Change in Properties of gas mixture.

$$\Delta U_m = \sum_{i=1}^{k} \Delta U_i = \sum_{i=1}^{k} m_i \Delta u_i = \sum_{i=1}^{k} N_i \Delta \bar{u}_i$$

$$\Delta H_m = \sum_{i=1}^{k} \Delta H_i = \sum_{i=1}^{k} m_i \Delta h_i = \sum_{i=1}^{k} N_i \Delta \bar{h}_i$$

$$\Delta S_m = \sum_{i=1}^{k} \Delta S_i = \sum_{i=1}^{k} m_i \Delta s_i = \sum_{i=1}^{k} N_i \Delta \bar{s}_i$$

We can write it as MiUi bar. Similarly, Hm is the enthalpy of the mixture. Summation is Hi, which we can write as MIHI, which is specific enthalpy, and this is molar enthalpy. We have multiplied molar enthalpy with mole, while specific enthalpy is multiplied by mass. So, you have to take a summation in each component, so number of components. Similarly, you will also get entropy. For example, if you have a mixture of A and B, which has 2 moles and 6 moles of B, and corresponding energy, antenna energy UA is given here, and UB is also given here, then we are simply adding the total energy of the mixture. Similarly, the way we are talking about the existential property, the absolute value, we can also make changes in the property, which will have delta U, so delta U is also your delta Ui, delta Hm is the summation of delta Hi. delta Sm is summation of delta Si and we will multiply it equal to mass i multiplied by delta U this is your specific internal energy this is specific enthalpy, specific entropy we will multiply it by mass of individual component similarly, if you have molar enthalpy or molar internal energy or molar entropy then you will multiply it by moles of individual component if we want it specific intensive properties. In this case, you will have to use mass fraction or mole fraction. If you are using mole fraction, then the molar internal energy of the mixture will be summation yi mole fraction multiplied by individual component molar internal energy. Similarly, the molar enthalpy of the mixture summation yi hi bar which is molar enthalpy of component i similarly if you can also extract entropy similarly if your intensity property is specific internal energy of the mixture means if you want to do the mixture then summation mass fraction component i multiplied by specific internal energy of component i similarly you can extract enthalpy and entropy Similarly, you can also extract specific heat decay, Cv and Cp, or you can extract it in kg form, specific form or molar form. Wherever you get molar form, you will use mole fraction, where you will get specific form, per unit mass, you will use mass fraction.

$$\Delta s_i = s^{\circ}{}_{i,2} - s^{\circ}{}_{i,1} - R_i \ln\left(\frac{P_{i,2}}{P_{i,1}}\right) \cong C_{p,i} \ln\left(\frac{T_{i,2}}{T_{i,1}}\right) - R_i \ln\left(\frac{P_{i,2}}{P_{i,1}}\right)$$

$$\Delta \bar{s}_i = \bar{s}^{\circ}{}_{i,2} - \bar{s}^{\circ}{}_{i,1} - R_u \ln\left(\frac{P_{i,2}}{P_{i,1}}\right) \cong C_{p,i} \ln\left(\frac{T_{i,2}}{T_{i,1}}\right) - R_u \ln\left(\frac{P_{i,2}}{P_{i,1}}\right)$$

$$P_{i,1} = y_{i,2} P_{m,2};\ P_{i,1} = y_{i,1} P_{m,1}$$

Let's move on. Now let's talk about Gibbs-Dalton’s law. Gibbs- Dalton’s law explains that in the ideal glass approximation, properties do not depend on the pressure of other gas components and normally the gas component behaves on the temperature of the mixture as you think that it is alone every component thinks that it is alone and it behaves accordingly so normally This can be extended for enthalpy, internal energy, Cv, Cp, etc. But it is a little different in entropy. In the case of entropy, we basically have to take partial pressure. We don't have to take the pressure of the mixture. That means, the delta S that you will extract, in this case, it is taking the mass, so delta Si is Si, since it is an idle gas, so Si is 0, 1, 2, minus this, and the second term is normally, rt ln p is written as r i ln pi 2 divided by pi 1 This term is the partial pressure of component i at state 2 and this is the partial pressure of component i at state 1 This part is the component i at state 1 and 2 So, there are 1 or 2 states and we are writing this as Cpi ln T2. So, this relation delta S, this is CPi ln Ti2 by Ti1. It means component i at state 2 and state 1 temperature. But this other part, the pressure that is visible here, this is partial pressure. To validate this. Partial pressure is the mole fraction multiplied by pressure of mixture in state 2. These are the two states. If your state is changing, then we will use it. Because we are taking out delta S, the state is changing. So, the pressure of the second state of the mixture. What is Pi1? multiplied by Pm mixture pressure in state 1. So, this is your general relation. Here partial pressure is used. In the same way, you can take out delta S per unit mole. This is a simple relation. The only difference is that your R has changed. Its unit will change. According to this, Ru will come. So, you can understand how much It is an interesting aspect that when we talk about enthalpy and entropy, you can take a simple temperature in this because enthalpy and enthalpy energy depend on simple temperature. But when we talk about entropy, it also depends on pressure. So, in such a case, what pressure to take, so pressure will come out. So, pay attention to this expression. Whenever you talk about entropy, about ideal gas, pay attention to this. If you talk about mixture, then you will pay attention to this. Now let's understand it after a question. So, this is the question, you have to extract exergy from this. This is the insulated tank. This is the insulated tank. It was divided into two compartments. One has oxygen and the other has CO2. One is 3 Kmol and the other is 5 Kmol. Both have initial temperatures of 25 degrees Celsius and the other is at the same pressure. Now we have removed the partition. and both the gases are allowed to mix sounding temperature is 25 degrees Celsius Both the gases are in ideal gas We have been asked the question of entropy change and energy destruction. These two things have been asked. Since energy is isolated, the energy destruction will be the same as energy generation. First, you will find out the energy change of each component. Or the total energy of delta S mixture. So delta Si is summation of delta Si And delta Si is Ni Delta Si is bar We are taking it as per unit mode So delta Ni If you see, in the last lecture I talked about this We will take this expression This is CPi ln Ti2 Ti1 minus Ru ln Pi2 by Pi1 Since the temperature is same, there is no change in temperature So the ratio is zero So this expression is Ni ln Pi2 by Pi1 was the initial compartment, so there is no problem. PI1 and PI, the initial PI is 200 only. And the final, because there is no difference in the pressure, so 200 only. The initial and final pressure will be the same. So, in this way, let's understand how to change this expression, how to simplify it. It has RU also, and minus also. Now I can remove this Ru. And Ni. I will write it like this. But the second state is in the mixture. So, I can write it like this. Component Yi2 Pm2. And this is Pi1. We can also write this as yi1. yi1 will be 1 because it was initially pure. Both these terms are the same so they will be cut. So, your expression of delta Sm will be minus Ru summation Ni ln yi. So, this expression is here. So Now From here you can take out the rest of the things. First you can take out the final mixture, how much Nm will be? Nm is NO2 plus NCO2 which is 3 plus 5... Kilomoles. I mean 8 Kilomoles. So, what is YO2? YO2 is now 3 by 8. 0.375. How much is YCO2? This is nCO2 divided by nm This is 5 by 8 Which is 0.625 So you have these two y's Now delta SM You can take out Minus Ru n O2 ln yO2 plus nCO2 Sorry, yeah, ln nCO2 ln Y CO2 When we plug in the relation, as you can see the Ru is 8.314 Kmol per Kelvin When we plug in the relation, it will come out to be 44.0 KJ per Kelvin So what is X-ray destruction? What will be X-Destruction? This is your T0 as generation. T0 is your 25 degrees Celsius, i.e. 298. Delta S generation which is the system that has been generated by the entropy which is the

Delta SM mixture or Delta S system which is 44.0 and if you plug in it, you will get 13.1 Mj so you can see that the amount is very big And this is the reason why you can understand that this is so much that you can't make it reversible. This is a highly irreversible process of mixing. so this was a simple expression.

Now let's move on to real gas mixtures. So, let's talk about real gas mixtures. The relation that we developed in Thamara earlier is also applicable in the real gas system.

$$dh_m = T_m ds_m + v_m dP_m$$

$$d(\sum mf_i h_i) = T_m d(\sum mf_i s_i) + (\sum mf_i v_i) dP_m$$

$$\sum mf_i \,(dh_i - T_m ds_i - v_i dP_m) = 0$$

$$dh_i = T_m ds_i + v_i dP_m$$

In fact, they are generic relations, so it is applicable everywhere. And if you apply this as TdS relation, then in dh is equal to Tds plus Vdp, you just apply m that dh of the mixture is equal to Tm of the mixture, dsm of the mixture plus Vm of the mixture and dp of the mixture. Means m is the condition of the mixture. With this you can show by applying this mathematical expression that with this you can derive that dhi is equal to Tm. dSi plus Vi dm. i means component. It means that this relation says that you normally gas, real gas. You can also use the component properties of the chart if you are evaluating the individual properties of the chart on Tm and Pm. But if you are using the chart, then the conditions of the chart are evaluated on Tm and Pm. But every component of Tr and Pr should be valid on Tm and Pm if you are talking about charts or generalize properties. Because it clearly shows that from this condition you can get out that dHi is enthalpy of a component i change in enthalpy of a component i is equal to Tm, temperature of the mixture multiplied by dSi plus Vi multiplied by dPm. If you have Pm and Tm, you can use Tr and Pr and chart. Or you can use equations of state and other things. If you have Vm and Tm, you can use Dalton's law and get PM. It is a little tricky in real gas mixtures, but if you have a chart, it is very easy. The second way is that you can use pseudo critical properties. You can take weight of critical properties and take out the pseudo critical properties of the mixture. Then you can use the chart and other properties. because the size of particles is different so the influence of particles is not that easy to predict many theories have been developed for this which you can read if you want but we will not discuss more in this lecture and the purpose of this lecture is to introduce how to calculate Dalton's law and how to use the Amagat’s law, how to use the property of the mixtures and especially what is important is how to extract Delta S for the idle gas mixtures and where the real gas comes, what are the ways to extract its deviation in which we have not done much practice in this lecture and we will not do much in this course but what is the direction to extract it, we have told you and you can also study for that You can learn about it in the course. So, this is the summary that we did in this lecture. We talked about composition, what is mass and mole fraction composition, how do you present it, we talked about PVT behavior, ideal gas mixture and real gas mixture, and how to extract its properties. We talked about this. So, I hope that you have come to this time of the lecture. And in next lecture we will talk about chemical reaction and thermodynamic equations and combustion. Till then I will take your leave. Namaskar.