Applied Thermodynamics for Engineers
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Lecture – 30
Behaviour of Gas Mixtures

Good morning everyone. Welcome to week number 10. We are in the last leg of our NOCC's course we have already covered 75% of the total content or maybe if we talk about the volume wise in course more than 80% but I know is it still which to go which is a one fourth of the entire course content. Now over last three weeks we have discussed about several application of thermodynamics. Because, you are talking about the course on applied thermodynamics.

Starting with the fundamental principles and a quick review of the fundamental principles of thermodynamics and a few initial concepts, we discussed about the options of estimating the properties of thermodynamic systems. Then we discussed about different kinds of power cycles, in the mode of gas powers cycles and also vapour power cycles. And for gas power cycles we have discussed about gas power cycle suitable for reciprocating devices and also gas Power cycle suitable for rotary devices. And for steam power cycle or vapour power cycle we have discussed primary about the Rankine cycle, which is again a rotary kind of cycle. And then of course we have discussed about the combined cycle also. Then after completing a discussion on all those power producing cycles, we have discussed about the power absorbing cycle which is the absorption refrigeration cycle and that one was covered in the previous week. So, now as we have decent idea about the possible kinds of refrigeration cycles, particularly the vapour compression and vapour absorption refrigeration cycles, probably the next logical step is to discuss about the air conditioning, because the biggest application area or I should say probably, the most explored application area of refrigeration is in the field of air conditioning. But again, refrigeration and air conditioning have one fundamental difference between them. Refrigeration, the primary objective as a defined in the first slide of the previous week, that the primary objective of refrigeration is to lower the temperature of zone or substance below the temperature of the surrounding and also maintain that low temperature.

Now, in air conditioning also we are actually just looking for reducing the temperature. In fact, if you think about our country point of view. Like we are talking about one country like India, there primary objective of refrigeration is to reduce the temperature, but that may not be case always like if you are talking about cold western country where the primary objective of air conditioning generally, becomes to heat the room or to maintain the interior temperature higher than the exterior. So, in the scope of air conditioning is not only cooling rather heating also comes into picture plus the temperature control is not the only objective rather you also want to control the humidity or moisture content of the interior air in case of air conditioning. Like in a moist are or somewhere the location where the humidity is quite high.

Like, we are recording this video sitting at IIT Guwahati which is at the Eastern side of India. In this zone generally the humidity content is quite high, in this zone in an air-conditioned space I should say we would like to reduce the moisture content and thereby reduce the humidity level. Whereas if you go to the northern part of the country where generally the moisture content is still quite low, it may be required to increase the moisture content increase the humidity of the interior. Therefore, the primary objective of air conditioning is to control both temperature and humidity level simultaneously. And there it is different from refrigeration. Of course, the way it is done that is nothing but refrigeration only but the way we said the lowest temperatures etc. they have certain relations with the control parameters. That is what level of temperature you want to achieve for what level of humidity we want to achieve in the conditioned space. So, whenever we are talking about an air conditioning application, we are actually talking about a mixture of two components. Like so far whatever we have discussed when we talked about the gas power cycles, we considered an ideal gas has a working medium.

When we talked about the vapour power cycles, we considered water vapour and also liquid water as the working medium. So, we always dealt with a single component. However, in case of air conditioning in fact in conventional refrigeration cycle also we dealing only with a single component, which is the refrigerant. That may have multiple phases, but is a single component.

But whenever you are talking about air conditioning application, we have to only deal with at least two components. One is the air which is often referred as and dry air and other is the water vapour the moisture. And though they both look to be in the gaseous phase but there is a between them. Like the dry air part that comprises of oxygen and nitrogen kind of gases which is extremely low boiling point. Therefore, whatever may be the low temperature that we can go for in practice, they will always remain as gaseous.

However, the water vapour that you are talking about that once we go below certain temperature that water vapour is start to condense and form liquid water. Thereby getting separated from the mixture. So whenever you are talking about an air conditioning application the primary thing for us to learn about the properties of a mixture which comprises of air, which is non condensable and also vapour which is condensable or to be more specific, I should say we have to talk about a mixture of a non-condensable gas and condensable vapour.

So, the study of air conditioning starts from the point of learning the properties of a gas-vapor mixture. But before learning about that probably it is logical to discuss about the properties of two component gas mixtures. And that is what you are going to talk about in this week, where we are going to talk about the mixture of gases and so far, we have dealt only with single component. So here we are trying to discuss about the properties of a multi component mixture where both the components are gases, that is both the components are non-condensable, both the components are the temperature levels will above their critical temperature.

And therefore, there is no chance for them to condense to form liquid. Both will continue to be in the gaseous space and accordingly whatever ways we can calculate the properties of the mixture that is something that you are going to explore in this week. The previous week we had quite a heavy discussion about refrigeration, we had four lectures or I should say three and half lectures, several kinds of refrigeration cycles were introduced and so to give you a bit of respite I had like to keep this week with short discussing very briefly about the properties of gas mixtures only the part which are relevant or which may be relevant for the practical application. And I shall be trying to restrict this only in two lectures only.

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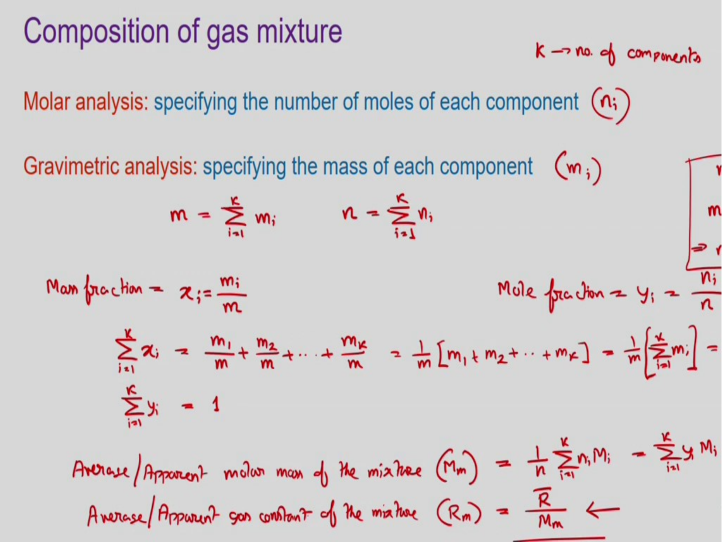

Composition of gas mixture

$k \rightarrow$ no. of components

Molar analysis: specifying the number of moles of each component (n_i)

Gravimetric analysis: specifying the mass of each component (m_i)

$$m = \sum_{i=1}^{k} m_i \qquad n = \sum_{i=1}^{k} n_i$$

Mass fraction $= x_i = \frac{m_i}{m}$

Mole fraction $= y_i = \frac{n_i}{n}$

$$\sum_{i=1}^{k} x_i = \frac{m_1}{m} + \frac{m_2}{m} + \dots + \frac{m_k}{m} = \frac{1}{m}\left[m_1 + m_2 + \dots + m_k\right] = \frac{1}{m}\left[\sum_{i=1}^{k} m_i\right] =$$

$$\sum_{i=1}^{k} y_i = 1$$

Average/Apparent molar mass of the mixture $(M_m) = \frac{1}{n}\sum_{i=1}^{k} n_i M_i = \sum_{i=1}^{k} y_i M_i$

Average/Apparent gas constant of the mixture $(R_m) = \frac{\bar{R}}{M_m} \leftarrow$

Firstly, let us try to identify what can be the composition of a gas mixture. Now to identify the composition of a gas mixture actually whenever you are talking about a gas mixture, we can always consider air as an example. Because as air generally comprises of oxygen and nitrogen which comprises more than 99% for in terms of volume and there can we small quantity of carbon dioxide and very less quantity of a few other gases.

And of course, in air we can also have water vapour in atmospheric air, but the discussion purpose, the air that we are taking as example that is devoid of any kind of water vapour that is it is only a mixture of oxygen nitrogen and a few other kinds of such gases. In fact, carbon dioxide is also not a non-condensable gas that can condense, because it is a critical temperature is quite low and therefore and if we pressurize here the carbon dioxide part may get separated from there. So here using the term air primarily we are referring to mixture of oxygen and nitrogen and maybe some similar gases. So, to discuss about the composition of a gas mixture we can go by two different approaches. One is the molar approach where we specify the number of moles for each component and other is a gravimetric approach where we specify the mass for each component. So, in case of molar approach let us say we are talking about a mixture which comprises of k number of components and each of these components are actually gases. For the moment you can assume into ideal gases there will be real gases as well, but still there all gases. So there, k number of components and we shall be using the subscript small i to denote the i^{th} component of the mixture.

Then when you are going for the molar analysis, we need to know the number of moles for each component. So, let us say n_i denotes the number of moles for the i^{th} component. Similarly, m_i denotes the quantity of mass for the i^{th} component. Then the total mass of this mixture is nothing but a summation of the mass of each of the components.

$$m = \sum_{i=1}^{k} m_i$$

Similarly, total number of moles in will be equal to:

$$n = \sum_{i=1}^{k} n_i$$

because again mass and moles they cannot be produced and are destroyed and therefore they remain conserved in a mixture. So, this way we have the total mass and total number of moles of the mixture. Now if we divide this mass of the i^{th} component by the total mass of the mixture then what we get that we call the mass fraction. Generally, denoted by symbols small x and subscribe i denote that is for i^{th} component. So, mole the mass fraction for the i^{th} component will be its own mass divided by total mass of the mixture.

$$mass\ fraction = x_i = \frac{m_i}{m}$$

Similarly, we can also define a mole fraction. Generally, the symbol y is used for that and it is the number of moles for the i^{th} component divided by the total number of moles.

$$mole\ fraction = y_i = \frac{n_i}{n}$$

So, in a mixture if we add up the mass fraction for all the components that what you are going to get, so if we write,

$$\sum_{i=1}^{k} x_i = \frac{m_1}{m} + \frac{m_2}{m} + \ldots\ldots\ldots\ldots + \frac{m_k}{m} = \frac{1}{m}[m_1 + m_2 + \ldots\ldots\ldots\ldots + m_k] = \frac{1}{m}\sum_{i=1}^{k} m_i = 1$$

In the same way can also get that the summation of i over the all the components of the mixture is equal to one. Quite often we define an average molar mass for the mixture. Average or sometimes also called apparent molar mass of the mixture and denoted by M_m. Here capital M denote the molar mass or molecular weight, also, you can call it for the small m mixture. Now, what is molecular weight or what is the relation between this small m_i and small n_i? The mass for the i^{th} component will be equal to the number of moles multiplied by the molecular weight for that component. Because molecular weight is defined as the mass per unit mole or the mass corresponding to one mole, so molecular weight can be denoted by this way. If you want to get the apparent molecular weight for the mixture then again, we have to use that relation of

$$\sum_{i=1}^{k} x_i = 1$$

Let us use this to write total mass for the mixture will be equal to:

$$m = \sum_{i=1}^{k} m_i = \sum_{i=1}^{k} n_i\, M_i$$

Now to get the apparent or average molar mass of the mixture then probably we can express this sum or total mass as the total number of moles multiplied by apparent molecular weight of this because small m will be equal to the total number of moles that are available in the mixture multiplied by the apparent molecular weight, so that should be equal to:

$$nM_m = \sum_{i=1}^{k} n_i\, M_i$$

And now if you divide this on both sides by this *n* then from there, we get the apparent molar mass of the mixture to be equal to:

$$Average\ or\ Apparent\ molar\ mass\ of\ the\ mixture, M_m = \frac{1}{n}\sum_{i=1}^{k} n_i\, M_i$$

and if you take this inside then this becomes:

$$= \sum_{i=1}^{k} y_i\, M_i$$

which is the apparent molar mass of the mixture. Be very careful, this is a nonphysical quantity, it is only a hypothetical concept. Because each of the component may have a molar mass of its own or each other components definitely has a molar mass of it is own. But for the mixture, there is no true molar mass this is only some sort of calculated, which generally allows us to calculate the average gas constant for the mixture. Like what is the relation between the molar mass and the gas constant, do you member? The ideal gas equation of state if you want to calculate? Or if R_i refers to the gas constant for the i^{th} component. Then, what is the relation of this one, the universal gas constant? The gas constant is defined as the universal gas constant divided by the molecular weight.

$$R_i = \frac{\bar{R}}{M_i}$$

The same is applicable here. So, if you want to write the average or apparent gas constant of the mixture, maybe we can use the symbol R_m that will be equal to:

$$Average\ or\ Apparent\ gas\ constant\ of\ the\ mixture, R_m = \frac{\bar{R}}{M_m}$$

So, from there also we can get the apparent gas constant for the mixture. And accordingly if he writes x_i we know:

$$x_i = \frac{m_i}{m}$$

in terms of molecular weight. We can always write this one to be equal to

$$= \frac{n_i M_i}{n M_m} = y_i \left(\frac{M_i}{M_m}\right)$$

So this is another relation between this molar analysis and the gravimetric analysis or you can say the mass fraction and mole fraction.

Now, this particular term is very important because you have already used this one. Where have you use this, the apparent gas constant for the mixture? You have solved several problems using the air standard assumptions or in those gas power cycles or air standard cycles we have always considered as the working medium which gives an ideal gas. And we have you used certain properties of air. There probably you have used that

$$R_{air} = 0.287 \text{ kJ/kgK}$$

Now from where this number came in? Because, air actually is only a mixture of gases, so this quantity came in by using this particular reduction. Where, for the mixture or apparent molar mass of the mixture comes from here. Primarily considering air as a mixture of 79% nitrogen and 21% oxygen by volume. Just put the numbers here, you know the molecular weight of oxygen and nitrogen and if you use 79% or 0.79 as the mole fraction for nitrogen and 0.21 for oxygen, then combining these two you can get the apparent molar mass. And using that you can get the apparent gas constant and that will be very close to this 0.287. So, this way we can have two different kinds of analysis for the gas mixtures.

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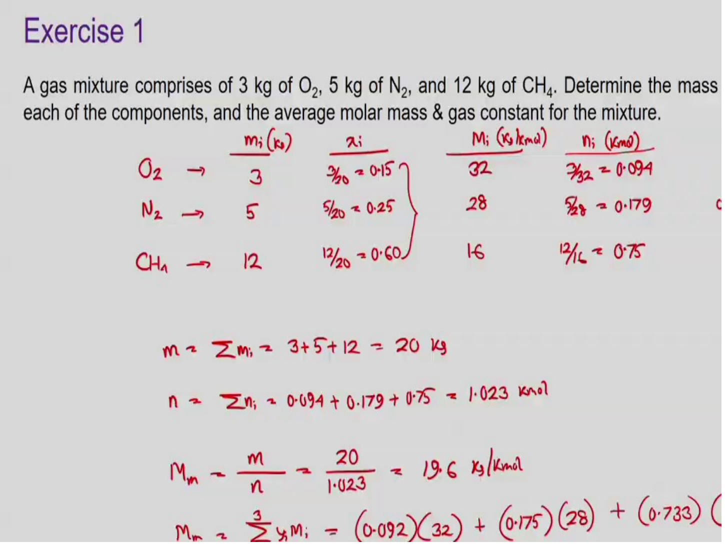

Exercise 1

A gas mixture comprises of 3 kg of O_2, 5 kg of N_2, and 12 kg of CH_4. Determine the mass each of the components, and the average molar mass & gas constant for the mixture.

	m_i (kg)	x_i	M_i (kg/kmol)	n_i (kmol)
O_2 →	3	3/20 = 0.15	32	3/32 = 0.094
N_2 →	5	5/20 = 0.25	28	5/28 = 0.179
CH_4 →	12	12/20 = 0.60	16	12/16 = 0.75

$$m = \sum m_i = 3+5+12 = 20 \text{ kg}$$

$$n = \sum n_i = 0.094 + 0.179 + 0.75 = 1.023 \text{ kmol}$$

$$M_m = \frac{m}{n} = \frac{20}{1.023} = 19.6 \text{ kg/kmol}$$

$$M_m = \sum^{3} y_i M_i = (0.092)(32) + (0.175)(28) + (0.733)($$

Before the proceed let us that quickly try to practice this one. We are talking about a gas mixture which comprises of three components. So, we have oxygen, nitrogen and CH_4 that is methane. So, their mass is given, so their mi in kg that is given. So, for oxygen it is given as 3, for nitrogen it is 5 and for methane it is 12. So, total mass of the mixture is equal to:

$$m = \sum_{i=1}^{3} m_i = 3 + 5 + 12 = 20\ kg$$

Then x_i the molar mass we have to divide the individual masses by the total mass, so it is equal to:

3/20 = 0.15 → O_2

5/20 = 0.25 → N_2

12/20 = 0.60 → CH_4

So, these are the corresponding molar masses. The mass fraction we have calculate for each of the component. There we have to get the mole fraction. To get the mole fraction we need to know their molecular weights. What is the molecular weight for oxygen? We can take it to

16 × 2 = 32 → O_2

14 × 2 = 28 → N_2

12 + 4 = 16 → CH_4

So correspondingly number of moles for each of them or maybe number of kilo moles if you want to check so it is always mass by molecular weight so it is:

3/32 = 0.094 → O_2

5/28 = 0.179 → N_2

12/16 = 0.75 → CH_4

By the way, what is the unit for this n_i and also what is the unit for this M which we have written earlier? The number of moles it is given in kmol. And what is the unit of molecular weight? Molecular weight is not a dimensionless quantity. So, we have use this one also earlier. That is the mass by unit mole so it will be equal to kg/kmol. But x_i and y_i of course are dimensionless quantities.

So now you know the exact number of moles for each component, so we have to get the y_i for that we have to get the total number of moles first. So, n is equal to:

$$n = \sum_{i=1}^{3} n_i = 0.094 + 0.179 + 0.75 = 1.023\ kmol$$

So, putting it there we can get the mole fraction y_i now:

$$0.094/1.023 = 0.092 \rightarrow O_2$$

$$0.179/1.023 = 0.175 \rightarrow N_2$$

$$0.75/1.023 = 0.733 \rightarrow CH_4$$

Summation of the three x_i and y_i values has to be equal to 1. Then may very small fractions because of the rounding off it. So, you know the mass and mole fraction for all the three components. Now we have to get the average molar mass and the gas constant for the mixture. So, average molar mass we can calculate as the total mass divided by total number of moles which is:

$$M_m = \frac{m}{n} = \frac{20}{1.023} = 1.96\ kg/kmol$$

there is another also you can do the same calculation.

How we can get this? Which is using this particular formula that is, you can also get this:

$$M_m = \sum_{i=1}^{3} y_i\, M_i = (0.092)(32) + (0.175)(28) + (0.733)(16) = 19.6\ kg/kmol$$

And finally, the R for the mixture, the gas constant or apparent gas constant for this mixture will be called universal gas constant divided by the apparent molar mass that we have calculated. Now what is the universal gas constant? The value, this only you should try to remember. It is:

$$R_m = \frac{\bar{R}}{M_m} = \frac{8.314}{19.6} = 0.424\ kJ/kgK$$

Be very careful the unit for *R bar* is 8.314 kJ/kmolK where as we a dividing it by molecular masses by kg/kmol, so the specific gas constant of a unit of kJ/kgK. So, this we can calculate the mass and mole fraction and also get some important parameter for the gas mixture.

Let us move to the *P-v-T* behaviour of a mixture. *P-v-T* refers to the relation between pressure, volume and temperature or, I should say the specific volume pressure and temperature. Now there are two kinds of relation generally we can go for any gas. For single gas if we are talking about, we can have two options.

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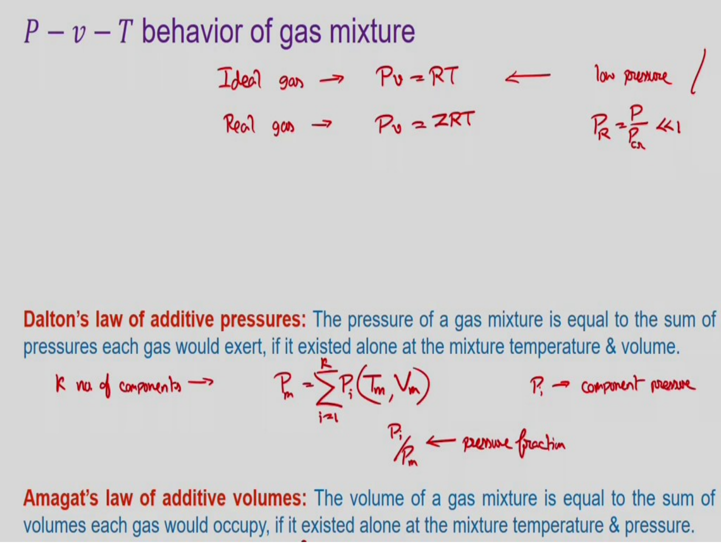

$P - v - T$ behavior of gas mixture

Ideal gas $\rightarrow$ $Pv = RT$ $\leftarrow$ low pressure /

Real gas $\rightarrow$ $Pv = ZRT$

$P_R = \frac{P}{P_{cr}} \ll 1$

Dalton's law of additive pressures: The pressure of a gas mixture is equal to the sum of pressures each gas would exert, if it existed alone at the mixture temperature & volume.

k no. of components $\rightarrow$ $P_m = \sum_{i=1}^{k} P_i(T_m, V_m)$

$P_i \rightarrow$ component pressure

$P_i / P_m \leftarrow$ pressure fraction

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

One is to go for the ideal gas. For ideal gas, we know that the equation of state or corresponding *P-v-T* relation is given as:

$$Pv = RT$$

where

v this a specific volume

R is a gas constant

And other is if you are talking about a real gas. For a real gas, we have already discussed about this one in week number 2. We generally introduced compressibility factor to get

$$Pv = ZRT$$

And how to calculate this compressibility factor, maybe to identify is using compressibility chart you already know. From the concept of critical pressure and critical temperature we can identify this z, compressibility factor. Now, any practical gases or real gases. approximate the ideal gas be here when the density is quite low. When the density is low the molecules of the gas are far apart from each other and therefore the presence of each molecule is not influenced by the presence of the surrounding molecules because the distance of intermolecular distance is too large to have any kind of realistic influence. And then in such situation in the real gas approaches ideal gas behaviour.

And in which situation we can have the density of a gas to be too low. Only if its pressure is small or its temperature is large. Therefore, any real gases approach the ideal gas behaviour when the pressure is low or the temperature is high. Now low temperature means how much lower talking about? You know this one we have discussed this again in week number 2, low pressure means is are talking about P_R the reduced pressure which is:

$$P_R = \frac{P}{P_{cr}} \ll 1$$

or it may be something the range of point 1 or 0.5. Then only we can talk that the pressure to be low. Similarly, high temperature means we are talking about the reduce temperature T_R that is:

$$T_R = \frac{T}{T_{cr}} \gg 2$$

preferably greater than 2 then only talk about high temperature. Therefore, the atmospheric temperature which maybe 300 K is a very high temperature for gases like a say hydrogen, which is an extremely low critical temperature. However, if we talk about water, which is a critical temperature of 647 K, then this atmospheric temperature is too small. Whereas for pressure again similarly we can identify this upon the critical pressure. So, when the density is low that is in terms of these conditions that we have just retained. We can assume the ideal gas behaviour. But sometimes the conditions are not in that range and therefore, we have to go for the real gas behaviour and we have also discussed about different kinds of options of identifying this compressibility factor. And also, the option of adopting the realistic gas equations something like a Vander Waal equation or real gas equations of state are a few others.

Now, when we are talking about a mixture of gases, if we mix a few ideal gases together then that mixture also should be like an ideal gas. Because again, once your mixing them together, it is very likely that despite being the mixture each of the molecules will be far away from each other and therefore it does not matter to it whether the neighbouring molecules of the same kind of different kind.

Like in air under the low-pressure high-temperature condition it is very likely that a particular oxygen molecule doesn't know in its neighbour what is it has. Another oxygen molecule or maybe nitrogen molecule or maybe carbon dioxide molecule and in such situation, you can easily assume that mixture also to behave like an ideal gas. And we can use this relation:

$$Pv = RT$$

where of course, R will be the R for the mixture, the gas constant for the mixture which can be calculated just following the process that we have just discussed. And also one another point that we have to keep in mind, the mixture that we are talking about that is a non-reacting mixture. There is no chemical reaction going on. Like if you are talking about a mixture of hydrogen and oxygen if the temperature level is high that we start to react together.

And in that situation, of course, it will not follow any kind of gas law behaviour. But as long as there is a non-reacting mixture, then a mixture of ideal gas should follow ideal gas behaviour only. Now in conjunction with this P-v-T relationship there are two laws that we generally study. This is the first one Dalton’s law of additive pressures, this one you must have learnt in school only which is also called the Dalton’s law of partial pressure.

Now, Dalton’s law of additive pressure though I must clarify the actual name should be the law of additive pressure because the term partial pressure is more relevant to ideal gases only. Now the Dalton’s law additive pressures say that the pressure of a gas mixture is equal to the sum of the pressures each gas will exert, if it existed alone at the mixture temperature and pressure.

That means suppose in a gas mixture, we are having a gas mixture at some temperature T_m and this mixture is occupying the total volume of V_m and it is a mixture of k number of components. We are having a gas mixture comprising of k number of components which is maintained at a temperature T_m and is occupying a volume of V_m. Now instead of maintaining the entire mixture, comprising of k components, if you pick up just one of the components from the mixture and remove everything else. Then if we allow a single component to occupy that entire volume that same V_m while maintaining at the same temperature Tm, then what pressure you have exert? Let us call that pressure say P_i. P_i of course that magnitude of the pressure depends upon the T_m and V_m.

Because if this compound gas is an ideal gas then it will follow the ideal gas behaviour and depending upon the value of its are R, T_m and V_m and this P_i will be decided. Similarly, each component would show a different value of this Pi because each having different value of R and it is a real gas definitely different value of the compressibility factor as well. So, from a mixture we are separating out of each component or leaving each of the component to occupy the same volume at the same temperature. Then each of them is showing different pressure than the Dalton law is pressure is that the pressure shown by the mixture will be nothing but:

$$P_m = \sum_{i=1}^{k} P_i\,(T_m, V_m)$$

this is what we referred as the Dalton's law of additive pressure.

Here this P_i is referred as the component pressure. And the second law, quite similarly it is called the Amagat's law of additive volumes. Amagat's law of additive volumes talks about the volume of a gas mixture and it says that the volume of the mixture will be equal to the sum of the volume each gas would occupy if it existed alone at the mixture temperature and pressure.

That means, again from that gas mixture comprising of k number of components let us say the mixture temperature is T_m and the pressure is P_m. Then from that mixture if we separate out one component and allowed it to be at the same temperature T_m and pressure P_m. Then the volume that it would occupy that volume may be given by symbol V_i, because again the magnitude of V_i will depend upon T_m and P_m and also the value of individual gas constant, R. Similarly, each of the component because they have different values of R and different values of Z in case of real gas. Then each of them is going to give you different value of this V. Then Amagat's is law of additive volume says that the total volume occupied by the mixture will be equal to the summation of all these component volumes. Here, this V_i is known as component volume.

So be very careful that the component pressure is evaluated by maintaining a constant temperature and constant volume or I should say the temperature same as a mixture temperature and volume is same as the mixture volume. Similarly, this component volume has been evaluated by maintaining the temperature same as the mixture temperature and pressure same as the mixture pressure.

Then the summation of component pressure gives you the total pressure of the mixture and summation of component volume gives the total volume of the mixture. Here this component pressure divided by the total mixture pressure is referred as pressure fraction.

$$Pressure\ fraction\ \rightarrow \frac{P_i}{P_m}$$

Similarly, the component volume divided by the mixture volume is known as this volume fraction.

$$Volume\ fraction\ \rightarrow \frac{V_i}{V_m}$$

Now if you are talking about an ideal gas, then an ideal gas follows both Dalton's law of additive pressure and Amagat's law of additive volumes exactly. I repeat ideal gases follow the Dalton's law of partial pressure and Amagat's law of additive volumes exactly. However real gases do not. They have some other factors that need to be added to this. As long as you are dealing with an ideal gas, you can blindly follow these two relations.

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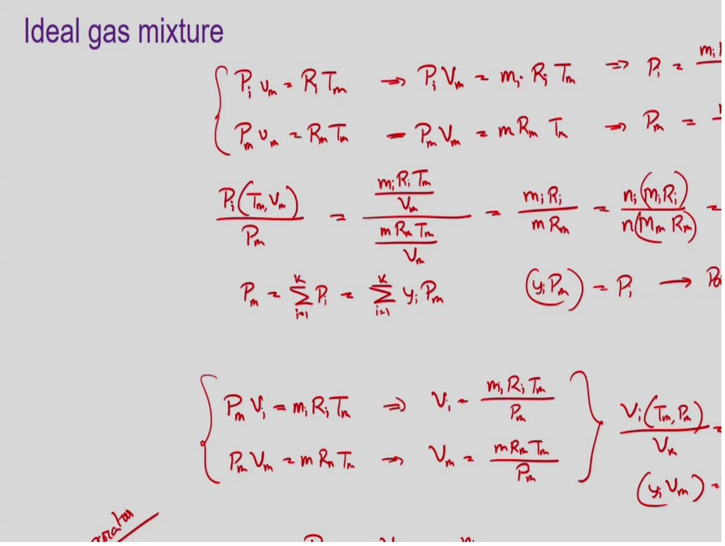

Ideal gas mixture

$$\begin{cases} P_i v_m = R_i T_m \Rightarrow P_i V_m = m_i \cdot R_i T_m \\ P_m v_m = R_m T_m \Rightarrow P_m V_m = m R_m T_m \end{cases}$$

$$\frac{P_i(T_m, V_m)}{P_m} = \frac{\frac{m_i R_i T_m}{V_m}}{\frac{m R_m T_m}{V_m}} = \frac{m_i R_i}{m R_m} = \frac{n_i (M_i R_i)}{n (M_m R_m)}$$

$$P_m = \sum_{i=1}^{k} P_i = \sum_{i=1}^{k} y_i P_m \qquad (y_i P_m) = P_i$$

$$\begin{rcases} P_m V_i = m_i R_i T_m \Rightarrow V_i = \frac{m_i R_i T_m}{P_m} \\ P_m V_m = m R_m T_m \Rightarrow V_m = \frac{m R_m T_m}{P_m} \end{rcases} \frac{V_i(T_m, P_m)}{V_m}$$

$$(y_i V_m)$$

Now, if you are going for an ideal gas mixture, for an ideal gas mixture, we know that each of the component is following the relation:

$$Pv = RT$$

Now if we talk about the i^{th} component then it is having the temperature may be the same as the mixture temperature, then it is having some value something like this:

$$P_i V_i = R_i T_m$$

and for the mixture:

$$P_m V_m = R_m T_m$$

Now from the Dalton's law of partial pressure if we write the component pressure, Dalton's law of additive pressure, if we write the expression for component pressure i.e., P_i which is this evaluated by this:

$$\frac{P_i(T_m V_m)}{P_m}$$

Now here we are talking about the i^{th} component maintained at the temperature T_m and volume V_m. So, for this i^{th} component this volume is V_m or let us say if we write in the total component this, we can write this one to be equal to:

$$P_i V_m = m_i R_i T_m$$

So, from there we can write,

$$P_i = \frac{m_i R_i T_m}{V_m}$$

This V we have to be careful this V is 'v' so here we can write this to be equal to:

$$P_m V_m = m R_m T_m$$

from there if we separate out P_m it will become,

$$P_m = \frac{m R_m T_m}{V_m}$$

So, if you put it back in this expression for the component pressure then we have,

$$\frac{P_i(T_m V_m)}{P_m} = \frac{\frac{m_i R_i T_m}{V_m}}{\frac{m R_m T_m}{V_m}}$$

so now if we separate this out that, T_m and V_m goes off, so we have:

$$= \frac{m_i R_i}{m R_m} = \frac{n_i(M_i R_i)}{n M_m R_m} = \frac{n_i \bar{R}}{n \bar{R}} = \frac{n_i}{n} = y_i$$

SO for ideal gas mixture, the component pressure is equal to the mole fraction. Now, this is applying the Dalton's law. So if we apply the Dalton's law of additive pressures then,

$$P_m = \sum_{i=1}^{k} P_i = \sum_{i=1}^{k} y_i P_m$$

This expression,

$$(y_i P_m) = P_i$$

is also called the partial pressure. And this term is used only for ideal gases not too much for real gases. This call the partial pressure.

Now if we do the same analysis from volume point of view, where we are allowing the *ith* component occupied the entire volume. We are maintaining the pressure and temperature constant for the i^{th} component and we are seeing what volume it occupies.

In that case it will be for the i^{th} component,

$$P_m V_i = m_i R_i T_m$$

From there, we can write:

$$V_i = \frac{m_i R_i T_m}{P_m}$$

Similarly, for the mixture we know

$$P_m V_m = m R_m T_m$$

so, we have,

$$V_m = \frac{m R_m T_m}{P_m}$$

if you combine this now:

$$\frac{V_i (T_m P_m)}{V_m} = \frac{n_i}{n} = y_i$$

Here similarly it is:

$$(y_i V_m) = V_i$$

is known as partial volume. So for ideal gases we used the term partial pressure to represent the component pressure and partial volume to represent a component volume. But for real gases generally don't use this partial term w is just stick with the terms: component pressure and component volume.

So, in a nutshell what you are getting for ideal gases, for ideal gases we saying that both Dalton's law of additive pressure and Amagat's law of additive volume are followed exactly. And from there we get that the component pressure divided by the mixture pressure is equal to the component volume by the mixture volume is equal to the mole fraction, that is y_i.

$$\frac{P_i}{P_m} = \frac{V_i}{V_m} = \frac{n_i}{n} = y_i$$

So, from the knowledge of mole fraction or from the knowledge of the molar composition of a gas mixture we can easily identify the partial pressure and partial volume for each of the components.

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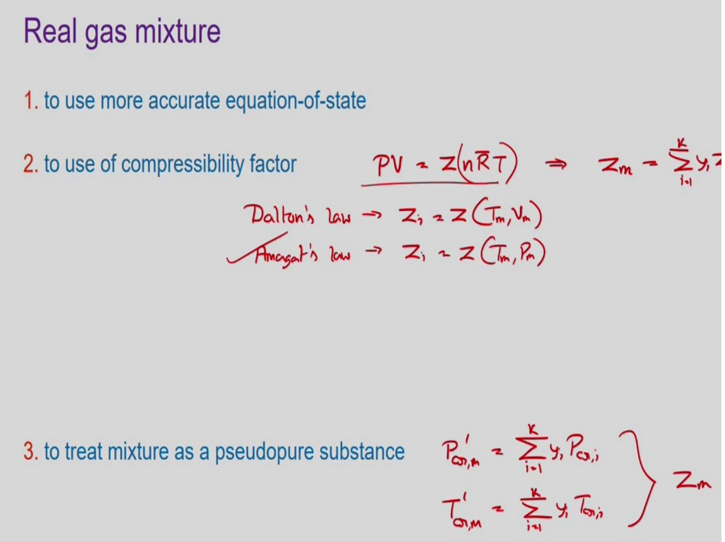

Real gas mixture

1. to use more accurate equation-of-state

2. to use of compressibility factor $PV = Z(n\bar{R}T) \Rightarrow Z_m = \sum_{i=1}^{K} y_i$

Dalton's law $\rightarrow Z_i = Z(T_m, V_m)$

✓ Amagat's law $\rightarrow Z_i = Z(T_m, P_m)$

3. to treat mixture as a pseudopure substance

$$\left.\begin{aligned} P'_{cr,m} &= \sum_{i=1}^{K} y_i P_{cr,i} \\ T'_{cr,m} &= \sum_{i=1}^{K} y_i T_{cr,i} \end{aligned}\right\} Z_m$$

Now, we go to the real gas mixtures. For real gas mixtures, before going that for ideal gas mixture suppose if you dealing with the mixture of gases which can dissolve like an ideal gas mixture, then how can you calculate this components? Because it is very difficult to have a direct measurement about the molar mass or I should say the mole fraction. Then this relation is very useful. We use an apparatus known as the Orsat apparatus. This orsat apparatus is you can visualise the one as the series of tubes and series of chambers maybe. Now the mixture of ideal gas maintains at constant pressure and temperature and also known volume, that is initially allowed to pass through one such compartment, where one of the component gases gets absorbed in certain chemical maintained there.

And once it comes out of there, then at the initial pressure and temperature is volume is measured then whatever volumes that will be less compared the initial one that corresponds to the component volume of that a component volume of that particular component which has been absorbed. This way by using suitable reagents we can keep on absorbing one of the components one by one and thereby we can get the measures of the partial volume for each of the components and as you know the total mixture volume then partial volume by the mixture volume gives you the mole fraction.

Now for real gases there are several approaches, as real gas does not follow the ideal gas equation of state so, we have to find some other options. Here Dalton's law and Amagat's law are also not exactly followed. The first option is to use more accurate equation of state. More accurate equation of state can be the Van der Waal equation of state, can be the

Redlich–Kwong equation of state and can be the Peng–Robinson equation of state. If you use some more accurate equation of state, which is the correct for that particular gas component that we talking about then you are definitely going to get much better result.

Second is to use the compressibility factor, now how to estimate the compressibility factor? For a real gas we know that we can always write,

$$PV = Z(n\bar{R}T)$$

where

Z is the compressibility factor

And from there, we have to identify a Z for the mixture, compressibility factor for the mixture. This Z_m can be identified in two ways: one if we go for the Dalton's law based approach. If we follow the Dalton's lower based approach then Z_i for each of the component is:

$$Z_i = Z(T_m\, V_m)$$

and from there we get the components and we get the total Z for the mixture which can be written as:

$$Z_m = \sum_{i=1}^{k} y_i\, Z_i$$

Like for every component this particular relation can be written, if we add of all the components of a mixture, we arrived at the above relation. And this Z_i we have to get either following the Dalton's law shown here or we may follow the Amagat's law also. If we follow the Amagat's law, in that case,

$$Z_i = Z(T_m\, P_m)$$

That is once we know the mixture pressure and temperature, then corresponding to the pressure and temperature we have to identify the value of compressibility factor from the compressibility chart and that we shall be to assigning Z_i. This way if we want to identify for all the components, then we shall be getting the value for that mixture. Generally, the Amagat's law has approach is more accurate here because Dalton's law neglect is the intermolecular attraction, as we talked about partial pressures here and Amagat's law talks about volume and therefore it is able to take care of the intermolecular attraction between molecules and is expected to give much better result. Therefore, Dalton's law is more suitable, as it neglects the intermolecular attraction so it is most suitable for low pressure applications, whereas the Amagat's law is most suitable for high pressure application because it is capable of taking care of the intermolecular forces which are more significant at higher pressures.

Thus, the third approach that is, to treat the mixture as a pseudopore substance. Now, what do you mean by a pseudopore substance? For a pseudopore substance we identify some pseudo critical pressure and temperature. The pseudo critical pressure for the mixture is given as:

$$P'_{cr,m} = \sum_{i=1}^{k} y_i \, P_{cr,i}$$

Similarly, pseudo critical temperature for the mixture is given as:

$$T'_{cr,m} = \sum_{i=1}^{k} y_i \, T_{cr,i}$$

and then we combine this. From this compressibility chart to get the Z for the mixture and once get Z_m, then we can go for the relation that is:

$$P_m V_m = Z_m RT$$

So, this is another approach where just be very careful about the difference between the approaches two and three. In approach number two, we are calculating Z for each of the components and then adding them up or I should say we are using relation:

$$\sum_{i=1}^{k} y_i \, Z_i$$

to get the Z_m. Whereas in case of the third approach we are calculating pseudo critical temperature and pressure for the mixture and then using that in the compressibility chart to get the Z_m. Let us see the application of this one in solving a problem. Here we are talking about a mixture comprising of one kmol of N_2 and 6 kmol of CO_2 at 300 K and 15 MPa. So, we have:

$T_m = 300$ K

$P_m = 15$ MPa

We have to obtain the volume of the tank considering three different ways here the term Kay's rule, it is actually this particular one is called the Kay's rule, which is the pseudopure approach. And generally, it has been found over a wide range of pressure and temperature it was found to be accurate within 10 %, which is acceptable in several practical applications.

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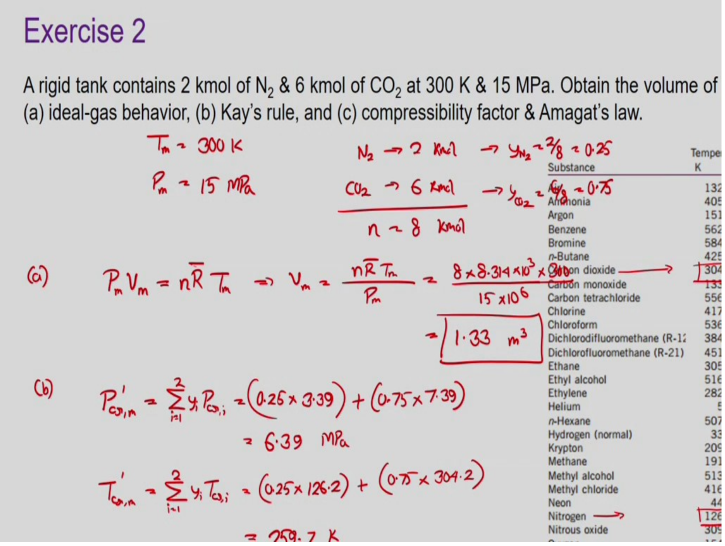

Exercise 2

A rigid tank contains 2 kmol of N_2 & 6 kmol of CO_2 at 300 K & 15 MPa. Obtain the volume of (a) ideal-gas behavior, (b) Kay's rule, and (c) compressibility factor & Amagat's law.

$T_m = 300\ K$

$P_m = 15\ MPa$

$N_2 \rightarrow 2\ kmol \rightarrow y_{N_2} = 2/8 = 0.25$

$CO_2 \rightarrow 6\ kmol \rightarrow y_{CO_2} = 6/8 = 0.75$

$n = 8\ kmol$

(a) $P_m V_m = n\bar{R}T_m \Rightarrow V_m = \frac{n\bar{R}T_m}{P_m} = \frac{8 \times 8.314 \times 10^3 \times 300}{15 \times 10^6}$

$= \boxed{1.33\ m^3}$

(b) $P'_{cr,m} = \sum_{i=1}^{2} y_i P_{cr,i} = (0.25 \times 3.39) + (0.75 \times 7.39)$

$= 6.39\ MPa$

$T'_{cr,m} = \sum_{i=1}^{2} y_i T_{cr,i} = (0.25 \times 126.2) + (0.75 \times 304.2)$

$= 259.7\ K$

Substance	Tempe K
Ammonia	405
Argon	151
Benzene	562
Bromine	584
n-Butane	425
Carbon dioxide	304
Carbon monoxide	133
Carbon tetrachloride	556
Chlorine	417
Chloroform	536
Dichlorodifluoromethane (R-1	384
Dichlorofluoromethane (R-21)	451
Ethane	305
Ethyl alcohol	516
Ethylene	282
Helium	5
n-Hexane	507
Hydrogen (normal)	33
Krypton	209
Methane	191
Methyl alcohol	513
Methyl chloride	416
Neon	44
Nitrogen	126
Nitrous oxide	309

And third, we have to use the compressibility factor calculated following the Amagat's approach. So let us try to follow the first approach. But before that we have

$$N_2 \rightarrow 2\ \text{kmol}$$

$$CO_2 \rightarrow 6\ \text{kmol}$$

so total,

$$n \rightarrow 8\ \text{kmol}$$

from there

$y_{N2} = 2/8 = 0.25$

$y_{CO2} = 6/8 = 0.75$

So, you know the mole fractions. So, let us now try to go for the first approach which is the ideal gas behaviour. For ideal gas behaviour, we can straight away go for assuming the mixture to be as we know that if we assume the gases to be ideal. then the mixture also be like an ideal gas. In that case, we can apply ideal gas equation of state for the mixture which is:

$$P_m V_m = n\bar{R}T_m$$

so, we have to get

$$= mR_m T_m$$

Now, this *n R bar* approach is quite advantageous because if you want to go by this approach, then first you need to know the mass for each of the components and also, we have to calculate R_m. Were *R bar* is a constant and therefore, it is always better if you know, the molar composition it is good to always go by this approach. So, from there,

$$V_m = \frac{n\bar{R}T_m}{P_m}$$

Values are all given, we have just put in the equation

$$= \frac{8 \times 8.314 \times 10^3 \times 300}{15 \times 10^6} = 1.33\, m^3$$

So, this is the volume corresponding to the ideal gas behaviour.

Next the case rule was shall be using the pseudo critical or pseudo potential. Now I should say we can, we shall use the pseudo critical values.

We need to identify the pseudo critical pressure and pseudo critical temperature for this mixture. For that purpose, we need to know the critical point values for the individual components. So, this is the table that we have used earlier also. Here our interest is CO_2 which is here. So, this is carbon dioxide in this table. So, these other critical points were for carbon dioxide and what about nitrogen? This is for nitrogen, so these are the critical point values for nitrogen.

So, $P_{pseudo\ critical}$ for the mixture of pseudo critical pressure for the mixture will be equal to :

$$P'_{cr,m} = \sum_{i=1}^{2} y_i\, P_{cr,i} = (0.25 \times 3.39) + (0.75 \times 7.39) = 6.39\, MPa$$

Similarly, the critical temperatures for the mixture or pseudo critical temperature for the mixture is:

$$T'_{cr,m} = \sum_{i=1}^{2} y_i\, T_{cr,i} = (0.25 \times 126.2) + (0.75 \times 304.2) = 259.7\, K$$

So, we have to now evaluate T_R and P_R for the mixture where,

$$T_R = \frac{T}{T'_{cr,m}} = \frac{300}{259.7} = 1.16$$

and

$$P_R = \frac{P}{P'_{cr,m}} = \frac{15}{6.39} = 2.35$$

So, the temperature is reduced temperature is not very high and also reduced pressure is quite high, it is definitely not an ideal gas mixture that we can see from here. Though we have solved the first part assuming ideal gas behaviour but here we can that T_R is not closed to 2 and P_R is extremely high.

And if we put this two values T_R and P_R in the compressibility chart, general compressibility chart, then we will be getting,

$$Z_m = 0.49$$

And from there, we get

$$V_m = \frac{Z(n\bar{R})T_m}{P_m}$$

which is nothing but

$$= Z(V_m)_{ideal}$$

calculated following the ideal gas behaviour and the result obtained is:

$$= 0.625\ m^3$$

Look at the difference from the previous one. So, it is about half than what we get in the previous that is simply because the; for the given conditions the gas mixtures is not at all behaving like an ideal gas mixture and therefore assume the ideal gas behaviour is always likely to give errors.

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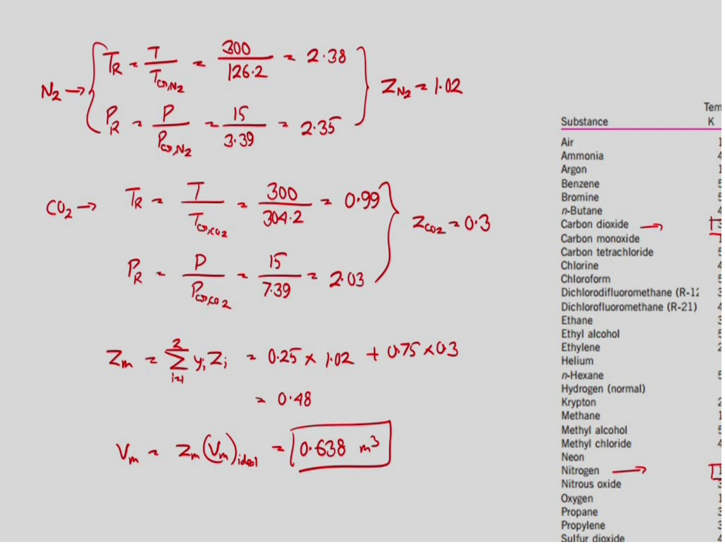

$$N_2 \rightarrow \left\{ \begin{array}{l} T_R = \dfrac{T}{T_{cr,N_2}} = \dfrac{300}{126.2} = 2.38 \\ P_R = \dfrac{P}{P_{cr,N_2}} = \dfrac{15}{3.39} = 2.35 \end{array} \right\} Z_{N_2} = 1.02$$

$$CO_2 \rightarrow \left. \begin{array}{l} T_R = \dfrac{T}{T_{cr,CO_2}} = \dfrac{300}{304.2} = 0.99 \\ P_R = \dfrac{P}{P_{cr,CO_2}} = \dfrac{15}{7.39} = 2.03 \end{array} \right\} Z_{CO_2} = 0.3$$

$$Z_m = \sum_{i=1}^{2} y_i Z_i = 0.25 \times 1.02 + 0.75 \times 0.3$$

$$= 0.48$$

$$V_m = Z_m (V_m)_{ideal} = \boxed{0.638\ m^3}$$

Substance	Tem K
Air	
Ammonia	
Argon	
Benzene	
Bromine	
n-Butane	
Carbon dioxide	
Carbon monoxide	
Carbon tetrachloride	
Chlorine	
Chloroform	
Dichlorodifluoromethane (R-1	
Dichlorofluoromethane (R-21)	
Ethane	
Ethyl alcohol	
Ethylene	
Helium	
n-Hexane	
Hydrogen (normal)	
Krypton	
Methane	
Methyl alcohol	
Methyl chloride	
Neon	
Nitrogen	
Nitrous oxide	
Oxygen	
Propane	
Propylene	
Sulfur dioxide	

And now the third part, where again we shall be using the critical point properties, but following Amagat's law-based approach, where we have to get that T_R and P_R for each of the components. So T_R first we calculate for nitrogen. For nitrogen,

$$T_R = \frac{T}{T_{cr,N2}} = \frac{300}{126.2} = 2.38$$

Then the P_R value:

$$P_R = \frac{P}{P_{cr,N2}} = \frac{15}{3.39} = 2.35$$

We can clearly see the component nitrogen though its reduced temperature is quite high the pressure is also high, so it is not behaving like an ideal gas. And as we combine this two we get Z for the nitrogen from this compressibility chart to be equal to:

$$Z_{N_2} = 1.02$$

It is quite closed to 1. So, it may be assumed to be behaving like somewhat like an ideal gas. Let us check out for CO_2, now for CO_2:

$$T_R = \frac{T}{T_{cr,CO2}} = \frac{300}{304.2} = 0.99$$

So, at the temperature point of view, it is far off and P_R is:

$$P_R = \frac{P}{P_{cr,CO2}} = \frac{15}{7.39} = 2.03$$

definitely the pressure is also coming to be quite high. Combining this:

$$Z_{CO_2} = 0.3$$

so though the nitrogen in a mixture is behaving something like an ideal gas. It is the carbon-dioxide part which far us from the others. And now we get Z of the mixture as:

$$Z_m = \sum_{i=1}^{2} y_i\, Z_i = (0.25 \times 1.02) + (0.75 \times 0.3) = 0.48$$

From there,

$$V_m = Z(V_m)_{ideal} = 0.638\, m^3$$

So just compare the value is 0.638 is quite close to the one got obtained from Kay's rule but far off from the ideal gas one. So, we have seen from the second approach that the mixture itself is not behaving some like an ideal gas because its reduce property values are far off from the corresponding condition. And in the second approach using Amagat's is law what we have done?

There we can clearly see that here the pressure and temperature values for the nitrogen is allowing it to be somewhat like an ideal gas, but CO_2 is the one which is far off from the ideal condition. And therefore the mixture is not behaving like an ideal gas behaviour.

Instead of Amagat's approach, you can also solve the same problem using the Dalton's approach you may get the similar values for this. So that is to the end of today's lecture where we have discussed about the mass and mole based approach for gas mixtures.

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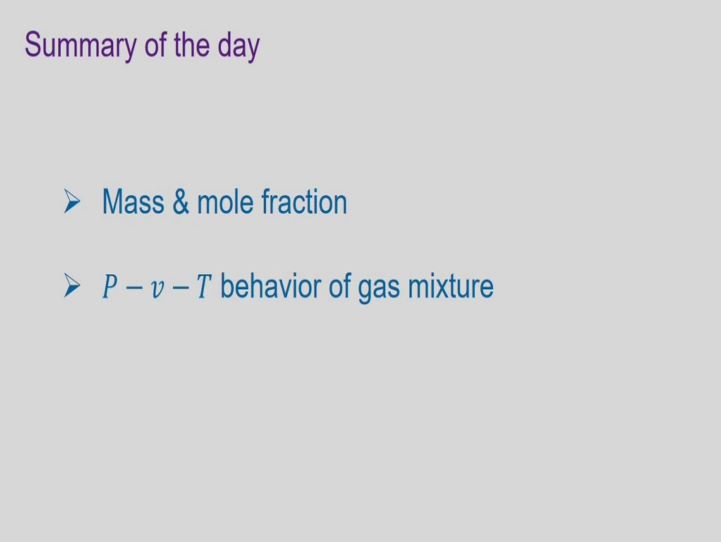

Summary of the day

- Mass & mole fraction
- $P - v - T$ behavior of gas mixture

We talked about the *P*-*v*-*T* behaviour of the mixtures where you have been introduced two laws: Dalton’s law of additive pressure and Amagat’s law of additive volume. And then we have seen how to apply them for ideal gas should be the cases and for real gas cases. So in the next lecture which I am expecting to be last for this week, I shall be talking about how to calculate other properties of a gas mixture assuming first ideal gas behaviour and then considering the real gas behaviour. Till then you please rehearse to the studies and go through this lecture. Thank you very much.