Advanced Thermodynamics and Combustion
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Module - IV
Properties of Gas Mixture
Lecture - 17
Ideal Gas Mixture

Dear learners, greetings from IIT Guwahati. We are in this course Advanced Thermodynamics and Combustion, module 4. The title of this module is Properties of Gas Mixtures.

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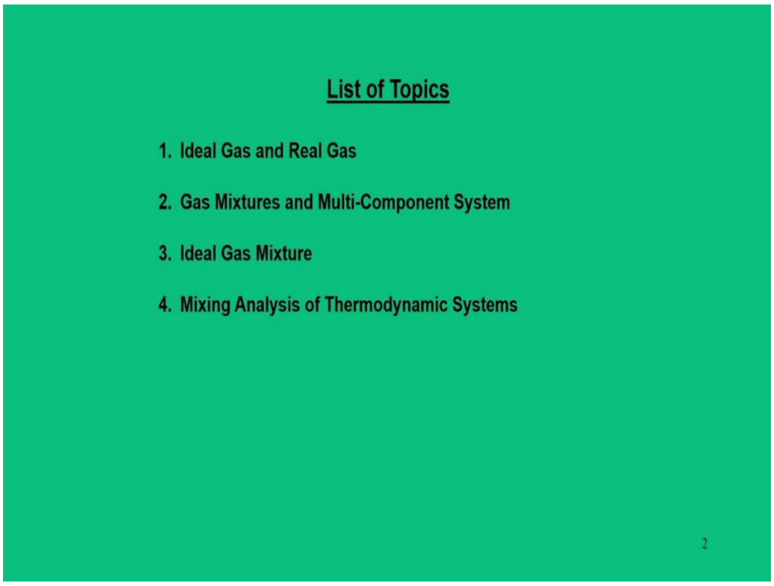

Prior to this, we have covered 2 lectures in this module first one is ideal gas and real gas, second one is a mixture analysis and multi-component systems. In today's lecture, we will focus our attentions only for Ideal Mixtures.

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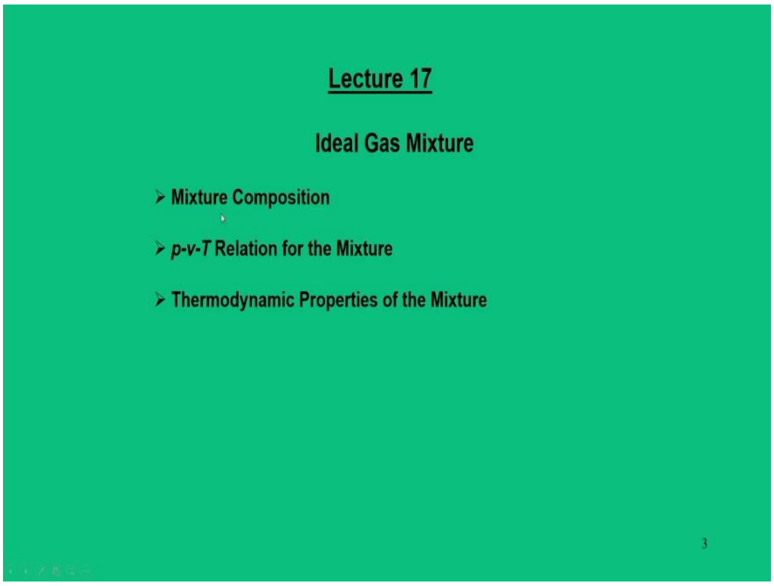

So, in this lecture we will concentrate the property evaluations for mixture containing ideal gases. To do that we require information about the composition of the mixtures and also we need to know the p-v-T, relation pressure volume and temperature relations for this mixtures.

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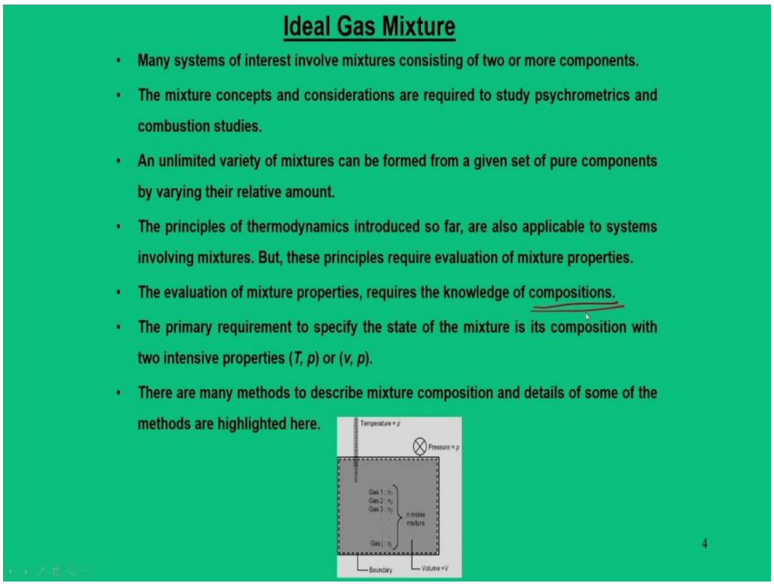

So, let us start with the first segment, that is ideal gas mixtures, that is under what circumstances a mixture we can treat it as an ideal gas model. First thing, I just want to emphasize is that prior to this we discussed about multi-component systems consisting of different phases of gases, different compositions. And, there are many ways this mixture or this system can be modeled. One of the simplest model is an ideal gas mixtures.

So, first thing is we need to freeze that the mixture has gaseous components and all these components, they behave as if they were in the ideal gas. So, we all know that for a pure component systems, we already derived the ideal gas models or we can say gas models. And, by doing so, we know all the properties for this individual components.

Now, when such components form a mixture, we need to treat them on individual basis and after that we will try to consolidate their entire information. And, try to see if the components after mixing they form a mixture which we are going to model as if it were supposed to behave as an ideal gas. So, this is the entire summary of this lecture. Now, let us see how you are going to do that.

Just to summarize few things that many systems of interest involve mixtures consisting of two or more components. The mixture components or considerations are required to study psychrometrics and combustion studies. Here, I need to emphasize that when you do this thermodynamics course and for undergraduate course, there we had some introductory topics like psychrometrics; that means, air and water vapors.

So, they behave as if they were having a mixture. So, under that circumstances also, you we use the concept of mixing analysis. And, apart from that in our study during the combustions when the reactants form the products, the reactant vanishes after the reaction is over and products gets generated. And, they form different gases or the products and all those gases form a mixture.

But, such a systems if we can do in an ideal gas model, it can give some realistic estimate. Then, the choice of preparing the mixture is very wide; that means, unlimited variety of mixtures can be formed from a given set of pure components and varying their relative compositions.

So, the principle of thermodynamics which are introduced so far is also applicable for systems involving mixture. The first thing that we need to know; that means, when you do this principle of thermodynamics, we need to know the two intensive properties.

And, typically it is temperature and pressure or specific volume and pressure. But, apart from that for mixing analysis, we require the composition of the components. So, this is the first thing or first important thing that we need to highlight, how you are going to decide about this compositions. And, these details are highlighted in the subsequent slides.

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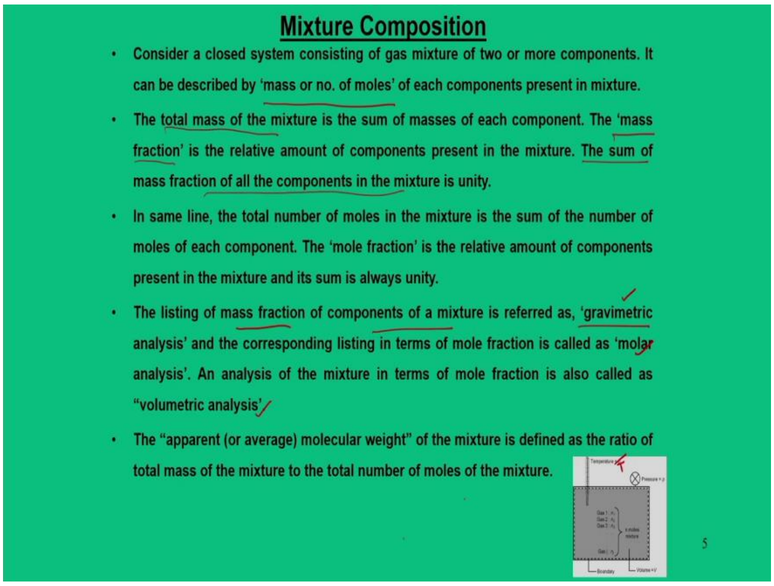

Now, if you consider a system consisting of mixture; that means, there are n number of gases, if you look at this figure. And, this gases they are treated as if they are in a temperature T and pressure p and each gases has different compositions. So, if you say total number of mixture is n moles and they occupy a volume V, then each of this component will have a number of moles as n_1, n_2, n_3 and n_i.

So, we introduce the concepts like mass or number of moles of each components in the mixture. Then, we need to nullify in a non-dimensional form, to do that we need to know the total mass of the mixtures. And, when you consider this total mass of the mixture it is nothing but the sum of the individual component masses. And, the mass fraction can be defined which is the relative amount of components present in the mixture.

Of course, the sum of these mass fractions for all the components in the mixture is unity. So, in the same line many a times in fact, instead of talking about mass, you talk about number of moles. Why? Because, when you talk about mass, we also need to know the molecular weight of each component plus we also need to the gas constant for each of these component.

But, rather if you use in terms of moles, the advantage that you will get is the consideration of mole fraction and 2 instead of gas constant, we can get this information through universal gas constant. Now, when you do this analysis, there are two types of analysis. When deal with the listing the mass fraction for the components of the mixture, we call this analysis as gravimetric analysis and the corresponding listing in terms of mole fraction is called as molar analysis.

So, in our study we will deal both the things. Like we can think about gravimetric analysis as well as the molar analysis. Many a times, molar analysis of the mixture is also called this volumetric analysis and other important point is that we need to find out the molecular weight of the mixtures. So, one way to do that is by considering through their respective mole fraction or mass fractions.

And, knowing their molecular weight of each individual components, one can find out the apparent or average molecular weight of the mixtures. And, it is defined as the ratio of total mass of the mixture to the total number of moles in the mixture.

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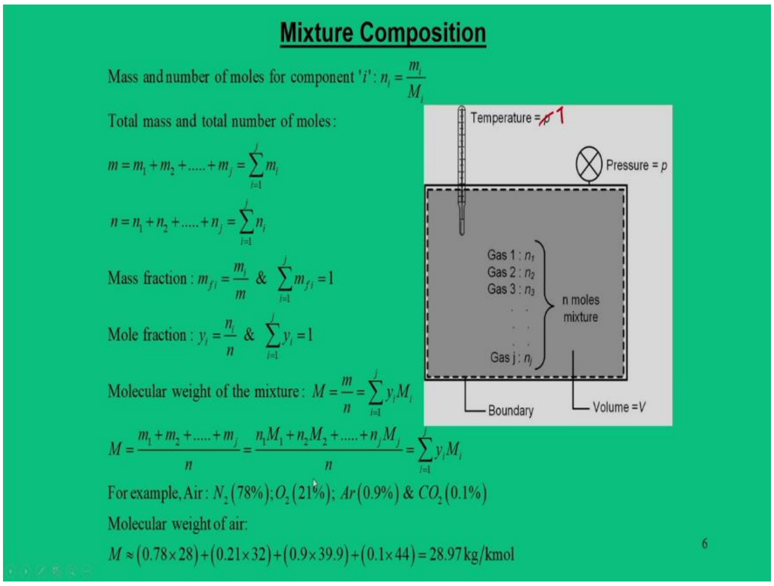

So, whatever I have discussed so far, this is represented in mathematical form in the slides. So, what it says is that we have a mixture containing number of gases 1, 2, 3 and j, each gas will have number of moles as $n_1, n_2, \ldots\ldots, n_j$. The total number of moles in the mixture is n and this mixture occupies a volume V and the mixer exists at temperature T and pressure p.

So, if under this situations, one can calculate the following:

$$m = m_1 + m_2 + \cdots .. + m_j = \sum_{i=1}^{j} m_i$$

$$n = n_1 + n_2 + \cdots .. + n_j = \sum_{i=1}^{j} n_i$$

$$\text{Mass fraction: } m_{f_i} = \frac{m_i}{m} \& \sum_{i=1}^{j} m_{f_i} = 1$$

$$\text{Mole fraction: } y_i = \frac{n_i}{n} \& \sum_{i=1}^{j} y_i = 1$$

$$\text{Molecular weight of the mixture: } M = \frac{m}{n} = \sum_{i=1}^{j} y_i M_i$$

$$M = \frac{m_1 + m_2 + \cdots .. + m_j}{n} = \frac{n_1 M_1 + n_2 M_2 + \cdots .. + n_j M_j}{n} = \sum_{i=1}^{j} y_i M_i$$

So, this is how we calculate the apparent weight or molecular weight of the mixture. For example, if you treat air is a mixture of nitrogen, oxygen, argon with this percentage, then one can find out the molecular weight by taking care of the relative weightage or compositions. And, we all know that this number is molecular weight of air is 28.97. So, this is how the mixture composition was analyzed.

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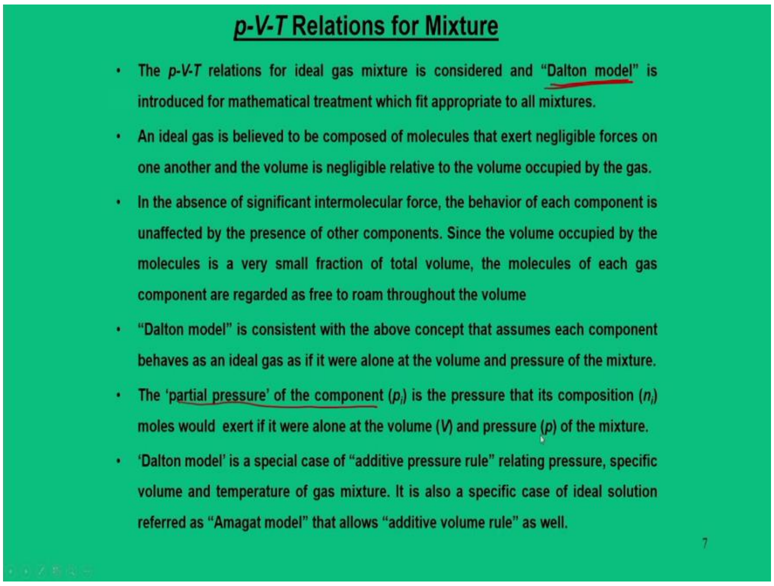

Then, we will move to pressure volume temperature relation for the mixtures. So, till this point of time, we all know that pressure volume temperature relations for pure components. Now, these pure components form a mixture. So, if the mixture behaves as if it is were a pure component and it consists of so many other pure components, then how you are going to deal with.

So, the first model that is proposed to for this analysis is the Dalton's model. So, this Dalton model is mainly used for an ideal gas model. What is the advantage of this model? Because, it gives a simplified mathematical treatment which can fit appropriate for all the mixture. Now, beginning we have assumed that the mixture behaves as an ideal gas as well as the pure components.

Now, when we say it is ideal gas model, at that point of time the first assumption that we make is that the molecules exert negligible forces on one another. And, the volume occupied by the molecule is negligible relative to the total volume occupied by this gas. Now, considering these two things; that means, in the absence of significant intermolecular forces, the behavior of each component is unaffected by the presence of other components.

At the same time, the volume occupied the by the molecules is very small as compared to the total volume. So, the molecules of these gas, thus can be regarded as to free to roam around throughout the volume. So, the Dalton's model takes this advantage of these considerations and they proposed a concept what we call as a partial pressure for the component of the mixture. So, considering this Dalton's model which is consistent with the above concept, it is assumed that each component behaves as an ideal gas as if it were alone at the volume and temperature of the mixture.

So, he defined this partial pressure of the component p_i is the pressure that its composition composition n_i moles would exert, if it were at volume V and pressure p of the mixture. But, the component p_i is the partial pressure of the component in the mixture. If this component with certain composition n_i is present in the mixture at a volume V; that means, V is the total volume of the mixture and the p is the total pressure of the mixture.

So, in that way the partial pressure for the component i is defined to some extent and it is a special case for additive pressure rule. Now, when you frame the additive pressure rule in your previous slides, main concentration was on the multi-component systems. But whereas, the Dalton's model is only for the ideal gas scenario. So, as a result what we see is that Dalton's model is a special case for additive pressure rule relating pressure, specific volume and temperature of the gas mixture.

And, it is also a specific case for an ideal solution, ideal solution is referred as Amagat model. Amagat model means it allows additive volume rule. So, additive volume rule gets simplified as Amagat model and additive pressure rule gets simplified as Dalton model for an ideal gas.

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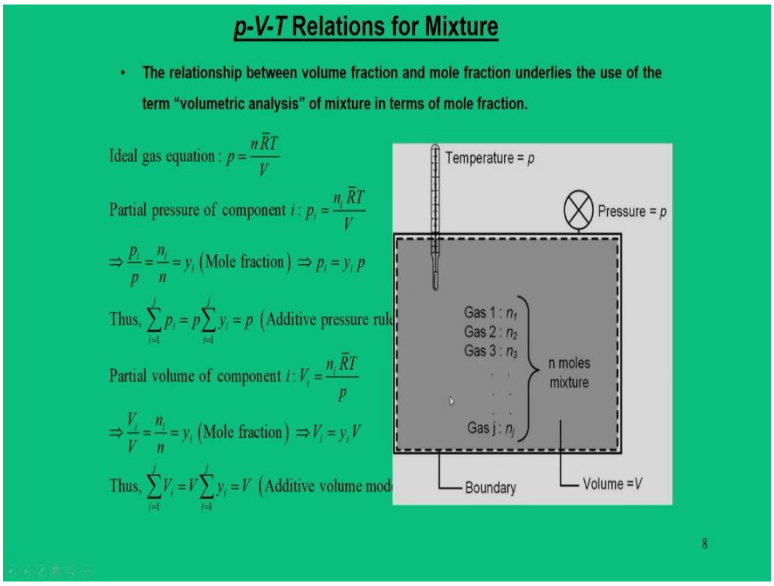

Now, considering the same concepts, we did it for calculation of mole fraction, mass fraction, molecular weight. We will try to see how to find out the partial pressure of the component. So, in a mixture, this mixture behaves as an ideal gas model. So, we can use this ideal gas equations $p = \frac{n\bar{R}T}{V}$.

Then, this equation we can write it for the component i, only change that is going to happen is the number of moles in that component, rest of the numbers remains same $p_i = \frac{n_i\bar{R}T}{V}$. Now, we can find a ratio $\frac{p_i}{p} = \frac{n_i}{n} = y_i \Rightarrow p_i = y_i p$. And, if you take the summation of this $\sum_{i=1}^{j} p_i = p\sum_{i=1}^{j} y_i = p$ which is nothing but your additive pressure load.

In same line, if you calculate the partial volume for the component i, $V_i = \frac{n_i\bar{R}T}{p}$. And, if you take the ratio $\frac{V_i}{V} = \frac{n_i}{n} = y_i$, we will also get the mole fraction and taking the summation of the individual volumes, then we will get the total volume $\sum_{i=1}^{j} V_i = V \sum_{i=1}^{j} y_i = V$. So, this analysis also satisfy the additive volume rule and this molar analysis we call this as a volumetric analysis of the mixture in terms of mole fractions.

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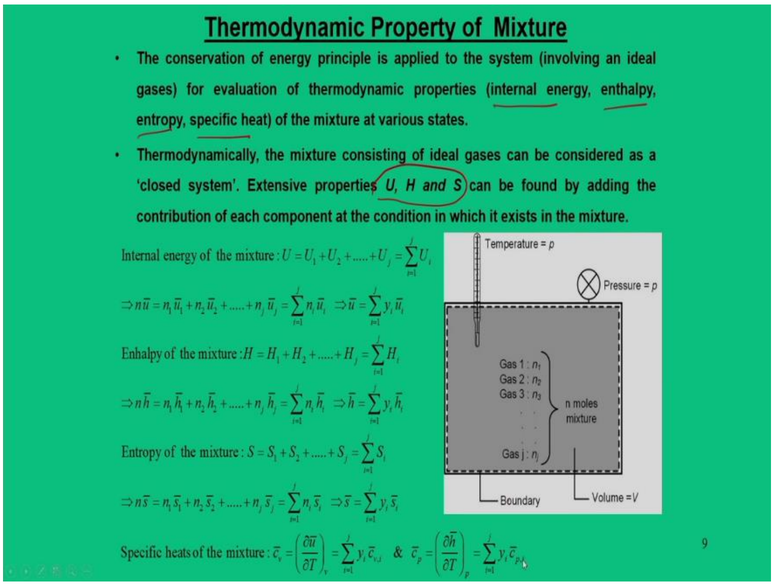

Now, having said this, we have individual component in terms of partial pressures. And, you also find out what is the volume of each individual component. Now, knowing all these things, we also know mass fraction as well as mole fractions. So, we can find out other properties of the mixture, I mean internal energy, enthalpy, entropy, specific heat.

And, thermodynamically we can view this as a closed system as shown in this figure, where there is no mass and energy interaction is taking place and from there we can find out the extensive properties U, H and S from this relations. So, with same philosophy internal energy of the mixture is the sum of internal energy of each component, $\bar{u} = \sum_{i=1}^{j} y_i \bar{u}_i$. And, $U = n\bar{u}$, $\bar{u}$ is the specific molar internal energy.

So, we can find out summation or you can find out $\bar{u} = \sum_{i=1}^{j} y_i \bar{u}_i$. In the same line, we can find out enthalpy of the mixture $H = \sum_{i=1}^{j} H_i$and $\bar{h} = \sum_{i=1}^{j} y_i \bar{h}_i$. Entropy of the mixture $\bar{s} = \sum_{i=1}^{j} y_i \bar{s}_i$. Specific heat that is specific heat at constant volume $\bar{c}_v = \left(\frac{\partial \bar{u}}{\partial T}\right)_v = \sum_{i=1}^{j} y_i \bar{c}_{v,i}$.

Then, specific heat at constant pressure; that means, it is a molar specific heat $\bar{c}_p = \left(\frac{\partial \bar{h}}{\partial T}\right)_p = \sum_{i=1}^{j} y_i \bar{c}_{p,i}$.

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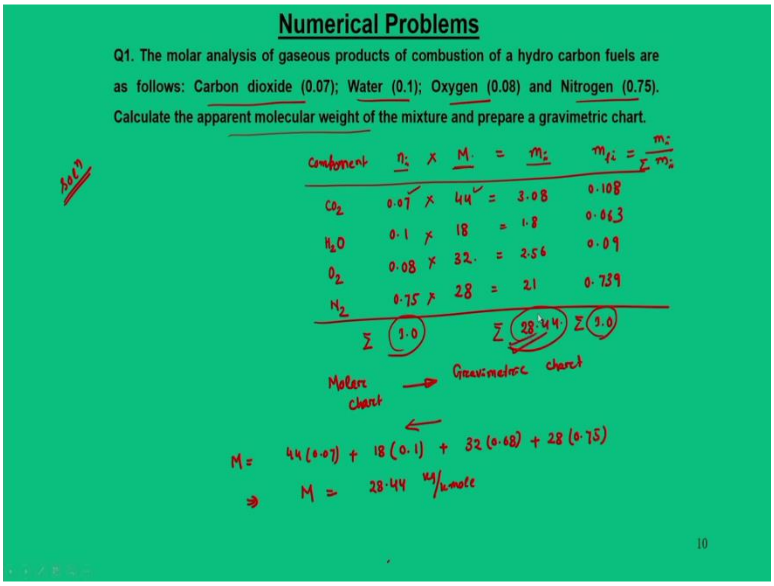

So, with this we are in the end of the discussions, that how you are going to get evaluate the thermodynamic properties of the mixtures. With this line, let us try to solve some numerical problems which we have understood from this lecture.

So, let us understand the first problem which states that the molar analysis of gaseous products of combustion for hydrocarbon fuels are listed as carbon dioxide as 0.07 fraction and water as 0.1, oxygen at 0.08, nitrogen at 0.75. And, if you add them together , you will land up having the total fraction as unity. So, this is nothing but your molar analysis.

Now, we are asked to find out the molecular weight of the mixtures and prepare a gravimetric chart. So, basically when you talk about gravimetric chart, we need to convert this molar analysis value to their respective mass fraction and see that if the total mass is unity or not. So, to start this first thing what we know is the mixture composition in terms of molar fractions; carbon dioxide, water, oxygen and nitrogen.

And, then we can prepare a chart consisting of component, then its mole fraction. Then, when we multiplied number of moles by molecular weight we get its mass. Then, from this we can also find out what is the mass fraction.

Component	n_i	M	$m_i = n_i \times M$	$m_{fi} = \frac{m_i}{\sum m_i}$
CO_2	0.07	44	3.08	0.108
H_2O	0.1	18	1.8	0.063
O_2	0.08	32	2.56	0.09
N_2	0.75	28	21	0.739
	$\sum n_i = 1.0$		$\sum m_i = 28.4$	$\sum m_{fi} = 1.0$

So, you can check your molar analysis also gives 1, $\sum n_i = 1$and this mass fraction analysis also gives $\sum m_{fi} = 1$. So, this analysis is correct. And this is called as gravimetric chart; that means, we converted molar chart to gravimetric chart. Now, if data is also given in the gravimetric form, we can get back to molar chart as well.

Now, what is left with, this apparent molecular weight. So, apparent molecular weight we can calculate. So, we know each of this molecular weight and their number of moles. So, we can write$\sum m_i = \sum n_i \times M_i = 28.44\ kg/kMol$. So, this is nothing but this data. So, this problem demonstrates about gravimetric chart and molar analysis or volumetric chart.

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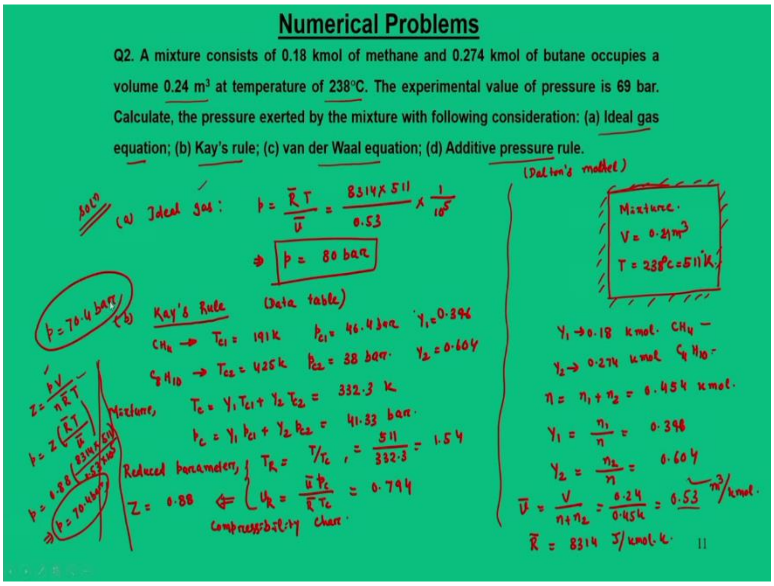

The next problem is about evaluation of pressure exerted by the mixture under the consideration of different rules. Like one is through ideal gas equation, other is Kay’s rule which we studied earlier, third one is van der Waal equations, fourth one is additive pressure rule. And, this additive pressure rule also closely resembles with the Dalton's model.

So, now we will try to evaluate them one by one. So, what the data that is given, a mixture consists of 0.18 kmol of methane (CH_4) and 0.274 kmol butane (C_4H_{10}) and it occupies a volume 0.24 m^3 and temperature 238C. So, you can recall that we have a container consisting of a mixture. And, it occupies total volume and temperature as 238C that is nothing but 511 K.

So, based on this we can find their respective molecular weight. Now, first thing that we need to find out what is the total number of moles; $n = n_1 + n_2 = 0.454\ kmol$. Now, then we can find out what is Y_1? Y_1 stands for methane, Y_2 stands for butane.

So, we can find out $Y_1 = \frac{n_1}{n} = 0.396$; $Y_2 = \frac{n_2}{n} = 0.604$. So, these are the common data we get. Also, we know volume, we can find out molar volume $\bar{v} = \frac{V}{n_1+n_2} = 0.53\ m^3/kmol$. And, we also know $\bar{R}$ is equal to 8314 J/kmol.K.

Now, let us start the first model, first model is ideal gas. So, ideal gas model says that we write the equation $p = \frac{\bar{R}T}{\bar{v}} = \frac{8314\times511}{0.53} \times \frac{1}{10^5} = 80\ bar$.

So, ideal gas model predicts that pressure exerted by the mixture will be 80 bar. Then Kay's rule talks about calculating the value with respect to critical parameter for the mixtures. So, first thing we need to find out the critical pressure and temperature for like for methane and butane. And, subsequently we have to find out critical pressure and temperature for the mixture.

So, we know that we have to use the data table.

$$CH_4: T_{c1} = 191\ K \quad p_{c1} = 46.4\ bar \quad Y_1 = 0.396$$

$$C_4H_{10}: T_{c2} = 425\ K \quad p_{c2} = 38\ bar \quad Y_2 = 0.604$$

So, then we can find out for mixture. For mixture, we can write $T_c = Y_1T_{c1} + Y_2T_{c2} = 332.3\ K$; $p = Y_1p_{c1} + Y_2p_{c2} = 41.33\ bar$. Now, you have to find the reduced parameter.

$$T_R = \frac{T}{T_c} = 1.54; V_R = \frac{\bar{v}p_c}{\bar{R}T_c} = 0.794; \;\; Z = 0.88\,(from\ compressibility\ chart)$$

$$Z = \frac{pV}{nRT}; p = Z\left(\frac{\bar{R}T}{\bar{v}}\right) = 70.4\ bar$$

So, Kay's rule gives p is equal to 70.4 bar.

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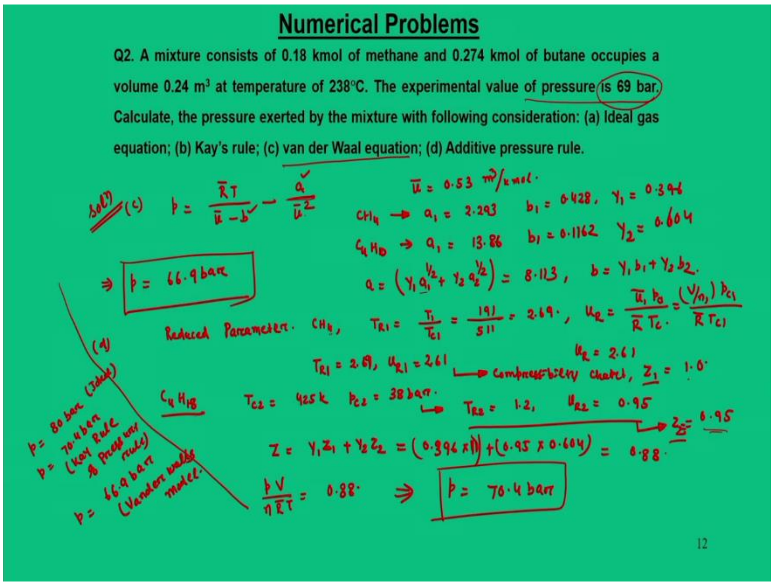

Then, we have to go for the van der Waal equation model. And in fact, this van der Waals model is one form of the real gas model.

$$p = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}^2}$$

$$From\ Data\ table: CH_4: a_1 = 2.293\ b_1 = 0.428\ Y_1 = 0.396; \qquad C_4H_{10}: a_1 = 13.86, \\ b_1 = 0.1162, Y_2 = 0.604$$

$$a = Y_1 a_1^{\frac{1}{2}} + Y_2 a_2^{\frac{1}{2}} = 8.113; b = Y_1 b_1 + Y_2 b_2$$

Why I said half?

Because, if you look at this equation, the empirical relation shows that it is related with $\bar{v}^2$. So, as if we have taken the square root of a_1. Then, after putting this number, we can get van der Waal gas model will give the pressure exerted by the mixture as 66.9 bar.

And, last one is additive pressure rule. Now, the additive pressure rule says that we have to treat each mixture component as individual component, calculate its critical values. Then, correspondingly you find its compressibility factor and then you calculate the effective compressibility factor. Then, from this effective compressibility factor, you have to calculate the pressure.

$$CH_4: T_{R1} = \frac{T_1}{T_{c1}} = \frac{191}{511} = 2.69; V_{R1} = \frac{\bar{v}p_{c1}}{\bar{R}T_{c1}} = 2.61;$$
$$Z_1 = 1.0 \ (from\ compressibility\ chart)$$
$$C_4H_{10}: T_{R2} = \frac{T_2}{T_{c2}} = 1.2; V_{R2} = \frac{\bar{v}p_{c2}}{\bar{R}T_{c2}} = 0.95;$$
$$Z_2 = 0.95 \ (from\ compressibility\ chart)$$
$$Z = Y_1Z_1 + Y_2Z_2 = 0.88$$

Then, we can write general equation that is $Z = \frac{pV}{nRT}; p = Z\left(\frac{\bar{R}T}{\bar{v}}\right) = 70.4\ bar$. So, if you can see that this is the same value what predicted by Kay rule. So, if you make a comparison of p, p is 80 bar which is predicted by ideal gas, p is equal to 70.4 bar which is predicted by Kay rule and pressure rule and p is equal to 66.9 bar by van der Waal's model.

So, of course, it is a real gas model. And, if you see the problem defines that experimental value is 69 bar. So, what we can say is that the van der Waal's gas model being a real gas approximation, its prediction is closer to experimental values. However, based on the simplicity, we are using ideal gas model.

And, based on our choice and advantage of the using different concepts, we can use the other models like Kay rule and pressure rules. So, this problem demonstrates that how the pressure of the mixture can be calculated by variety of considerations. With this, I conclude this lecture for today.

Thank you for your attention.