Applied Thermodynamic for Engineers
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Lecture – 31
Numerical Examples

Hello friends, welcome for the second time in this week where we are talking about the gas mixtures. In the previous lecture we have discussed about the possible scenario that we can have with a mixture of gases both ideal and real gases. And today which I will be using the discussion to calculate the properties of gas mixtures. Now to calculate the properties of gas mixtures we of course have to deal with two kinds of properties: one is extensive and other is intensive.

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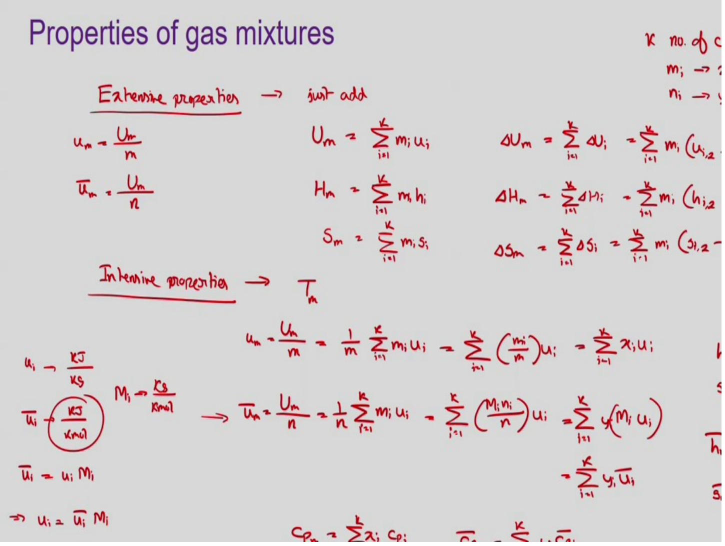

Properties of gas mixtures

k no. of

$m_i \rightarrow$

$n_i \rightarrow$

Extensive properties → just add

$u_m = \frac{U_m}{m}$

$\bar{u}_m = \frac{U_m}{n}$

$U_m = \sum_{i=1}^{k} m_i u_i$

$H_m = \sum_{i=1}^{k} m_i h_i$

$S_m = \sum_{i=1}^{k} m_i s_i$

$\Delta U_m = \sum_{i=1}^{k} \Delta U_i = \sum_{i=1}^{k} m_i (u_{i,2}$

$\Delta H_m = \sum_{i=1}^{k} \Delta H_i = \sum_{i=1}^{k} m_i (h_{i,2}$

$\Delta S_m = \sum_{i=1}^{k} \Delta S_i = \sum_{i=1}^{k} m_i (s_{i,2}$

Intensive properties → T_m

$u_m = \frac{U_m}{m} = \frac{1}{m}\sum_{i=1}^{k} m_i u_i = \sum_{i=1}^{k}\left(\frac{m_i}{m}\right)u_i = \sum_{i=1}^{k} x_i u_i$

$u_i \rightarrow \frac{kJ}{kg}$

$\bar{u}_i \rightarrow \boxed{\frac{kJ}{kmol}}$

$M_i \rightarrow \frac{kg}{kmol}$

$\rightarrow \bar{u}_m = \frac{U_m}{n} = \frac{1}{n}\sum_{i=1}^{k} m_i u_i = \sum_{i=1}^{k}\left(\frac{M_i n_i}{n}\right)u_i = \sum_{i=1}^{k} y_i (M_i u_i)$

$= \sum_{i=1}^{k} y_i \bar{u}_i$

$\bar{u}_i = u_i M_i$

$\Rightarrow u_i = \bar{u}_i M_i$

$c_{p_m} = \sum_{i=1}^{k} x_i c_{p_i}$

When we are talking about some extensive property, let us start with extensive property. For extensive properties the situation is very simple to identify the magnitude of any extensive property for the mixture we just have to add that corresponding extensive property for all its components. That is very simple. We just have to add for each of the components to get the final value of the extensive property for the mixture.

Let us say we talk about a mixture comprising of k number of components and m_i represents the mass of each of the components n_i represent the number of moles for each of the components corresponding you will have the mass fraction of x_i and mole function of y_i. And m is the total mass for the mixture where the summation is performed from i equal to 1 to k.

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

Whereas *n* is the total number of moles again summation is performed from *i* equal to 1 to *k*.

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

So, we now know the definition of this mass fraction and mole fraction, so I do not need to explain x_i and y_i. Some very common extensive properties that we can have let us say if you talk about *U*, what is *U* referring to? The internal energy of course *U* for the mixture can simply be written as:

$$U_m = \sum_{i=1}^{k} m_i u_i$$

where

u_i is the specific internal energy for that particular component

Similarly, if we write say enthalpy that again, very similarly,

$$H_m = \sum_{i=1}^{k} m_i h_i$$

h_i is the specific enthalpy for that particular component

And entropy can be expressed as:

$$S_m = \sum_{i=1}^{k} m_i s_i$$

Generally, these three are the most common extensive properties that you have to deal with in thermodynamics. Internal energy is related to the energy balance of application of first law of thermodynamics for a closed system. Enthalpy again, the application first law of thermodynamics, but for open system whereas entropy we have not used entropy that much in this course, but entropy is associated whenever you are looking for a second law analysis or exergy analysis. So, these three properties that we most commonly use, all of them are written in using capital letters and therefore they represent the extensive property of the mixture.

And this is the way we can calculate just by adding the contributions coming from each of the components. And quite often we may have to deal with the change in this properties. In fact in thermodynamics we hardly bother about the absolute magnitude of this properties rather we are always concerned about the change in this properties during the process or over a cycle. Then if ΔUm refers to the change in the mixture internal energy, it can be easily represented as:

$$\Delta U_m = \sum_{i=1}^{k} \Delta U_i = \sum_{i=1}^{k} m_i(u_{i,2} - u_{i,1})$$

Similarly, the change in enthalpy for the mixture can be written as:

$$\Delta H_m = \sum_{i=1}^{k} \Delta H_i = \sum_{i=1}^{k} m_i(h_{i,2} - h_{i,1})$$

And the same way we can write for the change in total mixture entropy as well.

$$\Delta S_m = \sum_{i=1}^{k} \Delta S_i = \sum_{i=1}^{k} m_i(s_{i,2} - s_{i,1})$$

Generally, we always go by these extensive notations for the mixture. Sometimes we may have to go for an intensive notation. In that case, if you want to define the specific internal energy for the mixture, then we can use 'u_m' which is nothing but:

$$u_m = \frac{U_m}{m}$$

where

U_m is the total energy of the mixture

Or if we want to define in a molar sense then it will be again:

$$\bar{u}_m = \frac{U_m}{n}$$

where

n is the total number of moles

Here this over bar notation represents the molar definition. Whereas the u_m without the over bar represents the mass base definition or the gravimetric definition. Similarly, we can also define the specific versions of the enthalpy and entropy for the mixture though we generally do not need to go by that route.

If now we want to define the intensive properties for the mixture. Most common intensive property is temperature and that if we can we easily understand. If suppose your mixing two gases and both of them at the same temperature, then you can expect the final temperature also be the same. Or other way actually that statement is not truly correct as we shall be correcting that later on. Let us come on from the other way around that is, if the mixture temperature is given, then you can easily assume that all the components are at the same temperature. So, for intensive sense we do not have to go for any calculation if temperature is given then you can easily calculate the temperature for each of the constituents because that will be equal to this temperature T_m only. Where T_m refers to the mixture temperature and also the component temperatures and this is applicable for both ideal and real gases.

Whatever you are writing in the slide they are applicable for both ideal and real gases. Now let us just go by the specific definition again. So u_m, the specification that is you know that the specification of any extensive property itself is an intensive property. So similarly, we should have written it here only,

$$u_m = \frac{U_m}{m}$$

and now if we expand the definition, we can write as:

$$= \frac{U_m}{m} = \frac{1}{m}\sum_{i=1}^{k} m_i\, u_i = \sum_{i=1}^{k}\left(\frac{m_i}{m}\right) u_i = \sum_{i=1}^{k} x_i\, u_i$$

In the same way we can write:

$$h_m = \sum_{i=1}^{k} x_i\, h_i$$

the specific version of the mixture enthalpy and specific version of the mixture entropy as:

$$s_m = \sum_{i=1}^{k} x_i\, s_i$$

Similarly, if you have to write in molar sense:

$$\bar{u}_m = \frac{U_m}{n} = \frac{1}{n}\sum_{i=1}^{k} m_i\, u_i = \sum_{i=1}^{k}\left(\frac{m_i}{n}\right) u_i$$

Before doing anything let us change this m_i to something, how can represent this in m_i, in terms of the number of moles or the molecular weight. When we that mi can be written as the molecular weight into the number of moles for this. So, this becomes:

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

But sometimes when we are writing the molar sense definition on the left inside each of the components also should be represented in terms of mole. So now here this u_i that is that you have written that is a specific internal energy for the component is written in mass basis. That is its unit is kJ/kg. Now, if you want to convert to mole, then what we have to do? u_i *bar* represents the specific internal energy per unit mole that is having the unit of kJ/kmol. Then what will be the relation between this u_i *bar* and this u_i? Of course, this:

$$\bar{u}_i = \frac{u_i}{M_i}$$

or I should write:

$$u_i = \bar{u}_i M_i$$

Now look at the expression that we have here, if we get them into one bracket then we have:

$$\sum_{i=1}^{k} y_i (M_i u_i) = \sum_{i=1}^{k} y_i \, \bar{u}_i$$

Earlier, I have made a mistake actually. What is the unit of molecular weight?

M_i → kg/kmol

if we multiply this u_i with m_i. Then what will be the final unit of this is kJ/kmol? That is this one only that is what we have here. And so,

$$\bar{u}_m = \sum_{i=1}^{k} y_i \, \bar{u}_i$$

Similarly,

$$\bar{h}_m = \sum_{i=1}^{k} y_i \, h_i$$

and

$$\bar{s}_m = \sum_{i=1}^{k} y_i \, s_i$$

here all the bar quantities represent the per unit mole definition, whereas the quantities same symbols represent without the bar represent per unit mass definition. So, this way we can calculate the specific values for each of the components. Two other intensive properties which are very important are specific heat, so, similarly C_p for the mixture just the way you have written for interspace internal energy or enthalpy or entropy. Just the same way we can write this one as:

$$C_{p,m} = \sum_{i=1}^{k} x_i \, C_{p,i}$$

And C_v, the specific heat at constant volume again can be represented as:

$$C_{v,m} = \sum_{i=1}^{k} x_i \, C_{v,i}$$

And similarly, we can also write the over bar quantities, that is the per unit mole definition,

$$\bar{C}_{p,m} = \sum_{i=1}^{k} y_i \, \bar{C}_{p,i}$$

C_p over bar for the highest component represents its specific heat on molar basis specific heat at constant pressure. Similarly, the isochoric specific heat for the mixture can be represented as:

$$\bar{C}_{v,m} = \sum_{i=1}^{k} y_i \, \bar{C}_{v,i}$$

So, the way we are calculate the properties both extensive and intensive here they are applicable for both real and ideal gas mixtures. Now let us reduce this to the specific case of ideal gas mixtures. We are going to apply these solutions for ideal gas mixture. Then we shall be moving to the real gas mixtures to see the same relations how can expand to the specific form for the gases.

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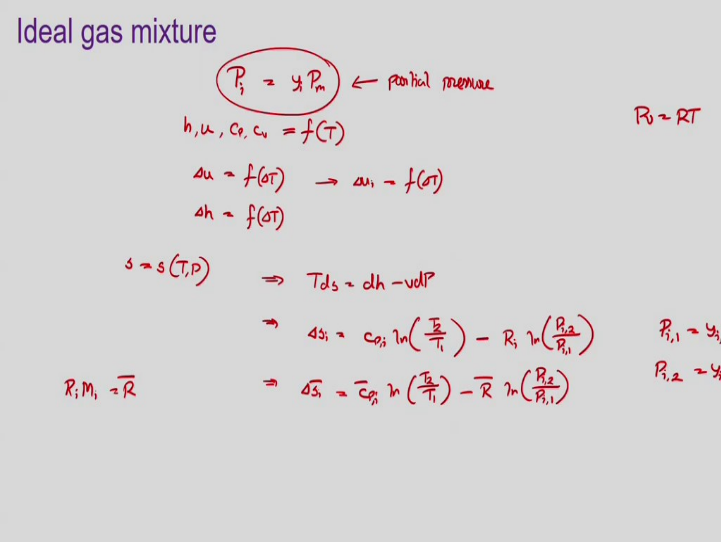

Ideal gas mixture

$\boxed{P_i = y_i P_m}$ ← partial pressure

$Pv = RT$

$h, u, c_p, c_v = f(T)$

$\Delta u = f(\Delta T) \rightarrow \Delta u_i = f(\Delta T)$

$\Delta h = f(\Delta T)$

$s = s(T, P) \Rightarrow T ds = dh - v dP$

$\Rightarrow \Delta s_i = c_{p,i} \ln\left(\frac{T_2}{T_1}\right) - R_i \ln\left(\frac{P_{i,2}}{P_{i,1}}\right)$

$P_{i,1} = y_i$

$P_{i,2} = y_i$

$R_i M_i = \bar{R}$

$\Rightarrow \Delta \bar{s}_i = \bar{c}_{p,i} \ln\left(\frac{T_2}{T_1}\right) - \bar{R} \ln\left(\frac{P_{i,2}}{P_{i,1}}\right)$

Now, when we are talking an ideal gas mixture, we know that the pressure for the i^{th} component can be represented as:

$$P_i = y_i P_m$$

where P_m is the mixture pressure and this P_i is known as the partial pressure. Because during yesterday's lecture we have seen that the component pressure which is nothing but

$$\frac{P_i}{P_m}$$

becomes equal to the partial pressure or

$$P_i \text{ becomes equal to } y_i P_m \text{ for ideal gases}$$

So, we use this sum partial pressure of partial volume only for ideal gases. Whereas generally you should call them component pressure. Like

$$\frac{P_i}{P_m} \rightarrow component\ pressure$$

and that definition is applicable for both ideal and real gases. Whereas for ideal gases which generally go with this partial pressure, where

$$\frac{P_i}{P_m} \rightarrow corresponding\ molar\ fraction = y_i$$

Now we also know that the common properties something like enthalpy, internal energy, C_p, C_v, etc, they are all functions of temperature alone for ideal gases. That is only for ideal gases their independent of pressure, they are functions of only temperature. This thing we are proved in a module number 2. I hope you remember or if you cannot remember properly you can go back to the corresponding lecters are concerned chapter in the textbook. Where from here we know that enthalpy, internal energy, C_p, C_v etc, they are all function of temperature alone for ideal gases. Whereas for real gas they are functions of both temperature and pressure. Now as they are functions of temperature alone, therefore any change in them like change in internal energy should be function of corresponding change in temperature or similarly change in specific enthalpy that is should be a function of the change in temperature. Therefore, if we know the change in temperature, we should be able to identify the corresponding change in this property values same for C_p and C_v. We just need to know the relation between u and T which you already know from the P-v-T relationship.

Once we know the P-v-T relationship for ideal gases, we know the P-v-T relationship is given as:

$$Pv = RT$$

Then you already know what is the relation between pressure and from where we can get the expression for this or we can just use the value of the specification and we can go by the route also. The situation is not that straight forward for entropy of course.

Because, even for ideal gaseous also entropy is a function of both temperature and pressure. What was the relation, do you remember? $T\mathrm{d}s$ relations or using $T\mathrm{d}s$ relation you can get the definition of entropy as a function of temperature and pressure. Do you remember the forms? We have to start with that $T\mathrm{d}s$ relation something like

$T\mathrm{d}s = \mathrm{d}h - v\mathrm{d}P$.

Then use the thermodynamic property relations and using the Maxwell's equations, we get equations of for ideal gases specifically. Something like that change in specific entropy can be written as:

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

Here 2 and 1 refers to the final state initial state respectively. Here we are writing this for the change in specific entropy for the i^{th} component. If you can evaluate the change in all the components these by just adding them together, we can get the final change in the mixture. Whereas in this case, we can always write:

$$\Delta u_i = f(\Delta T)$$

Because as we have mentioned that all the components are filling the temperature at the same way. So, the change in temperature is the same for all the components and therefore here writing T_1 and T_2 instead of T_{i1} and T_{i2} in the change in entropy equation, we can write as:

$$\Delta s_i = C_{p,i}\, ln\left(\frac{T_2}{T_1}\right) - R_i\, ln\left(\frac{P_{i,2}}{P_{i,1}}\right)$$

as they are in thermal equilibrium at both state 1 state 2. But this P_{i2} and P_{i1} can be different because as this relation shows us so,

$$P_{i,1} = y_{i,1}P_{m,1}$$

Similarly

$$P_{i,2} = y_{i,2}P_{m,2}$$

this way we can calculate the change in entropy for the i^{th} component. If you want to write this one in molar sense, then just dividing everything in terms of moles we can write this one as:

$$\Delta \bar{s}_i = \bar{C}_{p,i}\, ln\left(\frac{T_2}{T_1}\right) - \bar{R}\, ln\left(\frac{P_{i,2}}{P_{i,1}}\right)$$

Here we are actually multiplying everything is the molecular weight, then,

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

So, this way we can convert the same definition to the molar scale as well. This we can calculate the change in all the five most important thermodynamic properties for an ideal gas mixture.

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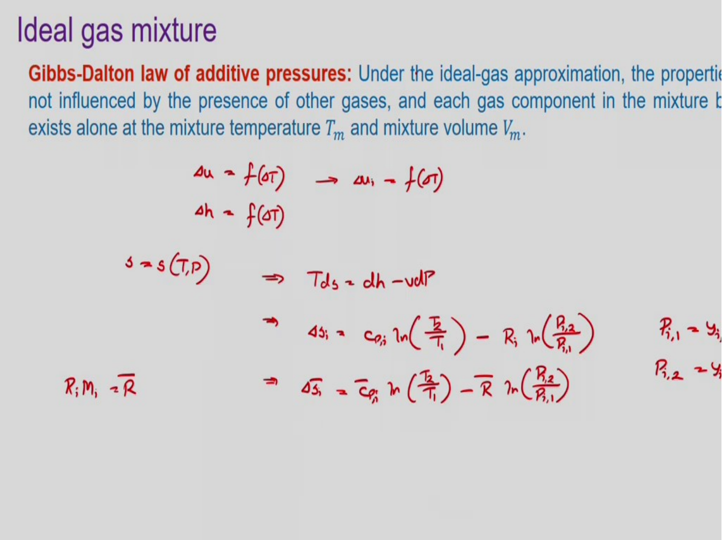

Ideal gas mixture

Gibbs-Dalton law of additive pressures: Under the ideal-gas approximation, the properti
not influenced by the presence of other gases, and each gas component in the mixture b
exists alone at the mixture temperature T_m and mixture volume V_m.

$$\Delta u = f(\Delta T) \rightarrow \Delta u_i = f(\Delta T)$$

$$\Delta h = f(\Delta T)$$

$$s = s(T,P) \Rightarrow T\,ds = dh - v\,dP$$

$$\Rightarrow \Delta s_i = c_{p,i} \ln\left(\frac{T_2}{T_1}\right) - R_i \ln\left(\frac{P_{i,2}}{P_{i,1}}\right)$$

$$P_{i,1} = y_i$$

$$P_{i,2} = y_i$$

$$R_i M_i = \overline{R}$$

$$\Rightarrow \Delta \overline{s}_i = \overline{c}_{p,i} \ln\left(\frac{T_2}{T_1}\right) - \overline{R} \ln\left(\frac{P_{i,2}}{P_{i,1}}\right)$$

Here, this particular relation that we use here is often known as a Gibbs-Dalton Principle or Gibbs-Dalton law of additive pressures. I should have in a way not have written this one as Gibbs-Dalton law of additive pressure, it is more like Gibbs-Dalton principle which states that: under ideal gas approximation the properties of a gas does not influence the presence of other gases and each gas component the mixture behaves as if it exist alone in the mixture temperature T_m and mixture volume V_m. So, the gas molecules you probably can remember that ideal gas approximation we take when the gas molecules whose density is extremely low that is either at low pressure or at high temperature.

So, that gas molecules are far apart from each other and therefore each molecule is not at all influenced by its neighbouring molecules. Because of neighbouring molecules is far apart to put any kind of influence on this. And therefore, the way single ideal gas behaves, a mixture of ideal also be as the same way. And therefore, the properties of not at all influence by the presence of other gases and each gas component in the mixture behaves like it is staying alone at the mixture temperature and mixture volume. From there we can calculate the pressure of the mixture for this.

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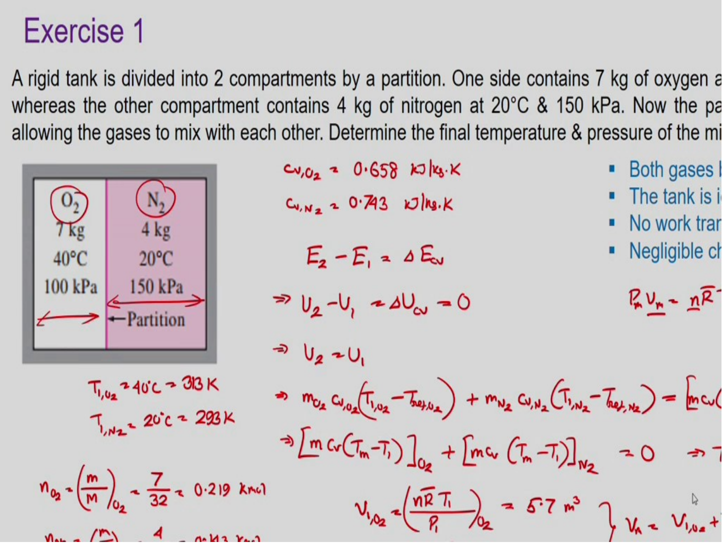

Exercise 1

A rigid tank is divided into 2 compartments by a partition. One side contains 7 kg of oxygen a
whereas the other compartment contains 4 kg of nitrogen at 20°C & 150 kPa. Now the pa
allowing the gases to mix with each other. Determine the final temperature & pressure of the mi

- Both gases
- The tank is i
- No work trar
- Negligible ch

$c_{v,O_2} = 0.658$ kJ/kg.K

$c_{v,N_2} = 0.743$ kJ/kg.K

$E_2 - E_1 = \Delta E_{cv}$

$\Rightarrow U_2 - U_1 = \Delta U_{cv} = 0$

$\Rightarrow U_2 = U_1$

$\Rightarrow m_{O_2} c_{v,O_2}(T_{1,O_2} - T_{ref,O_2}) + m_{N_2} c_{v,N_2}(T_{1,N_2} - T_{ref,N_2}) = [mc_v($

$\Rightarrow [m c_v(T_m - T_1)]_{O_2} + [m c_v(T_m - T_1)]_{N_2} = 0 \Rightarrow$

$T_{1,O_2} = 40^\circ C = 313\,K$

$T_{1,N_2} = 20^\circ C = 293\,K$

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

$n_{O_2} = \left(\frac{m}{M}\right)_{O_2} = \frac{7}{32} = 0.219$ kmol

$V_{1,O_2} = \left(\frac{n\bar{R}T_1}{P_1}\right)_{O_2} = 5.7\ m^3$ } $V_m = V_{1,O_2} +$

Let us try to solve one example to apply the same principle. Here we are talking about a rigid tank; I have the diagram here. It is divided into two compartments by partition, one side contains 7 kg of oxygen. This is having 7kg of oxygen at 40 ^{0}C and 100 KPa. On the other side we have nitrogen, 4 kg of nitrogen, the one shown in pink at 20 ^{0}C and 150 kPa.

Now, the partition has been removed, allowing the gases to mix with each other. We have to determine the final temperature and pressure of the mixture. So, this problem is very straight . The initial state for both the components are given. Initially they are unmixed but at the end of the process there mixed with each other. So, we have to get this final temperature and pressure once they are fully mixed to each other that is they have been in some kind of equilibrium. Now to start with, we have to analyse whether we are dealing with ideal gases are real gases. For that, how we can identify whether the given conditions oxygen and nitrogen or ideal gas or real gas? You know that we have to check their P_r and T_r values. Pressures and temperatures for both the components are given and you can get the corresponding critical point values, say for oxygen and also for nitrogen.

And for oxygen at 40 ^{0}C, first it should be converted to Kelvin and then divided by the critical temperature of oxygen to check whether this value is close to 2 or not. Similarly, the 100 kPa pressure has to be divided by the critical pressure for oxygen to check whether it is an extremely small number or not. Repeat the same procedure for nitrogen.

And in this case both gases you will find that both gases should be like an ideal gas. And therefore, their mixture also should be treated as an ideal gas mixture. Now we are assuming the tank to be ideally insulated, has no information given about any heat interaction with the surrounding. So we are assuming the tank to be insulated and no work transfer involved and your also change neglecting any changes in kinetic and potential energies.

So, we know some properties the specific is that I am going to use here is:

$c_{v,O2}$ = 0.658 kJ/kgK

$c_{v,N2}$ = 0.743 kJ/kgK

So, how can you calculate this? We have to applying an energy balance on this one? Show let us say E_1 is the initial state and E_2 is the final state, then this is a transient process. So, over the entire process if we write the first law of thermodynamics the answer is found.

$$E_2 - E_1 = \Delta E_{control\ \ volume}$$

Now here we are neglecting the changes in kinetic and potential energies, so we can also write:

$$U_2 - U_1 = \Delta U_{control\ \ volume}$$

Now the system is ideally insulated and also there is no work transfers, that means there is no heat interaction and work interaction with the surrounding.

Then the total internal energy for this system or control volume should remain the same over the entire process which gives us:

$$U_2 = U_1$$

Now initially, what is your internal energy? And finally, what is the internal energy that we have to identify? So initially U_1 refers to oxygen and nitrogen being separated. So for U, we can write:

$$m_{O2}c_{v,O2}(T_{i,O2} - T_{ref,O2}) + m_{N2}c_{v,N2}(T_{i,N2} - T_{ref,N2})$$

where the first term of the above equation is the initial internal energy for the oxygen part and second term is the initial internal energy for nitrogen part.

This sum should be equal to that of the mixture. And in the mixture as you know that both components remain separately, so we can treat them separately also, we can write:

$$[mc_v(T_2 - T_{ref})]_{O_2} + [mc_v(T_2 - T_{ref})]_{N_2}$$

i.e.,

$$m_{O2}c_{v,O2}(T_{i,O2} - T_{ref,O2}) + m_{N2}c_{v,N2}(T_{i,N2} - T_{ref,N2}) = \left[mc_v(T_2 - T_{ref})\right]_{O_2} + \left[mc_v(T_2 - T_{ref})\right]_{N_2}$$

If we reorient them now, we can probably write it as:

$$[mc_v(T_2 - T_1)]_{O_2} + [mc_v(T_2 - T_1)]_{N_2} = 0$$

Now T_2 is a final temperature, while initially they are separated, so, T_1 for oxygen and T_1 for nitrogen are different, but their T_2 has to be same. So, this T_2 let us called this T_m which is the mixture temperature. Now mass for both the components are given, for oxygen mass is 7 kg, for nitrogen it is 4kg, C_v I have given to the values, T_1 for oxygen in this case is equal to 40 ^{0}C that is, 313 K, T_1 for nitrogen is equal to 20 ^{0}C that is, 293 K. Putting everything together we are going to get,

$$T_m = 32.2\ ^0\text{C}.$$

So, we have got the mixture temperature. Now to get the mixture pressure, to get the mixture pressure, we need to know the mixture volume. We do not know the volume, once we have the temperature and volume both we can go for the ideal gas equation of state over the mixture. Hence, we can write something like say,

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

but T_m we have calculated what you need to know is P_m and V_m. So, let us calculate the total number of moles involved here.

$$n_{O_2} = \left(\frac{m}{M}\right)_{O_2} = \frac{7}{32} = 0.129\ kmol$$

$$n_{N_2} = \left(\frac{m}{M}\right)_{N_2} = \frac{4}{28} = 0.143\ kmol$$

So, the total number of moles for the mixture:

$$n = n_{O_2} + n_{N_2} = 0.362\ kmol$$

So, we have the total number of moles, this one and now I have to get the total volume. Now total volume we have already learned the Amagat's law also the Dalton's law of partial pressure. So, we can also say that the total volume has to be equal to their component volumes.

So, what is individual volume? V1 for oxygen, we know the mass and other things. so from where we can easily calculate it should be equal to:

$$v_{1,O_2} = \left(\frac{n\bar{R}T_1}{P_1}\right)$$

Now number of moles of oxygen we have calculated *R bar* is a universal gas constant T_1 and P_1 are a given, so putting that it will be coming as:

$$= 5.7 \text{ m}^3$$

and

$$v_{1,N_2} = \left(\frac{n\bar{R}T_1}{P_1}\right)_{N_2}$$

$$= 2.32 \text{ m}^3$$

Now, look at this, here this $V_{1,O2}$ refers to the volume for this side of the compartment and $V_{1,N2}$ refers for the volume for this side of the compartment. And once you have removed the partition both the gases are mixed with each other and therefore the total mixture is able to occupy the entire chamber that is both the compartments together. So, what should we have V_2 or V_m? It should be equal to:

$$v_m = v_{1,O_2} + v_{1,N_2}$$

$$= 8.02\, m^3$$

So, from there, we can get:

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

$$= 114.5 \text{ kPa.}$$

So, this we can calculate for an ideal gas mixture the final pressure temperature and any other properties you want.

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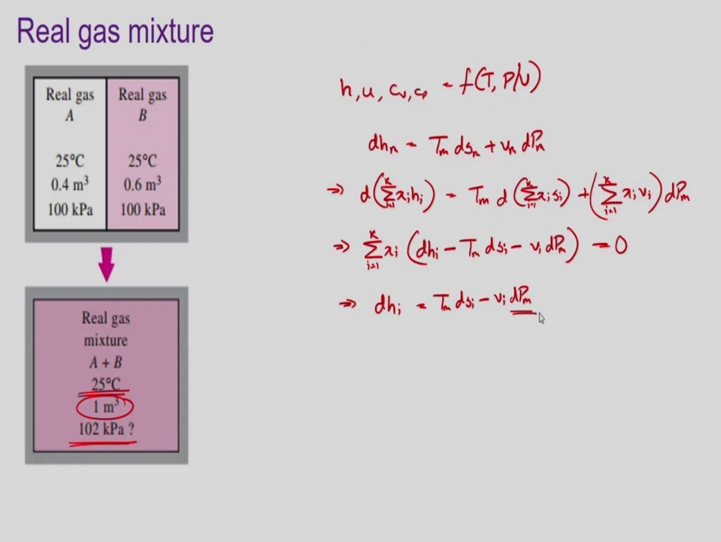

Real gas mixture

$$h, u, c_v, c_p = f(T, P/V)$$

$$dh_m = T_m ds_m + v_m dP_m$$

$$\Rightarrow d\left(\sum_{i=1}^{k} x_i h_i\right) = T_m d\left(\sum_{i=1}^{k} x_i s_i\right) + \left(\sum_{i=1}^{k} x_i v_i\right) dP_m$$

$$\Rightarrow \sum_{i=1}^{k} x_i \left(dh_i - T_m ds_i - v_i dP_m\right) = 0$$

$$\Rightarrow dh_i = T_m ds_i - v_i \underline{\underline{dP_m}}$$

Now let us quickly move to the real gas mixtures. Here we have a situation for a real gas mixture, we have gas A and gas B. Their initial conditions are given, both are at the same temperature and pressure. But their volumes are different: 0.4 m^3 for gas A and 0.6 m^3 for gas B. Now they are allowed to mix with each other, just like the previous question that we have solved.

Both the gases are now occupying the entire compartment and therefore the final volume is given which will be equal to the initial volume of 0.4 m^3 for gas A plus 0.6 m^3 that is total 1 m^3. And also, as both are at the same temperature, their temperature may be same their volume is definitely 1 m^3, but what will be the pressure? Should the pressure will remain at 100 kPa?

If they are ideal gases then it should remain at 100 kPa, but if they are real gases like in this example it may not be 100 kPa, it may be something like this, it may be higher or lower. Therefore, for real gases we cannot separately analyse both the components rather we have to combine all of them together. Because for real gases we know that all these properties:

$$h,\ u,\ C_v,\ C_p = f\,(T,\ P \text{ or } V)$$

temperature and either pressure or volume should be specified, one of them is necessary. So, it is a function of two of the given components. And entropy was of course already a function of both the components. So now if we write, say, the second law of thermodynamics using the *Tds* relation of second law of thermodynamics for the mixture, probably you can remember that earlier we had this *Tds* relation:

$$dh_m = T_m ds_m + v_m dP_m$$

we have written this one for the mixture now. You know the expression for hm and these components, so the above equation can be expressed in the summation of components form as:

$$d\left(\sum_{i=1}^{k} x_i\, h_i\right) = T_m\, d\left(\sum_{i=1}^{k} x_i\, s_i\right) + \left(\sum_{i=1}^{k} x_i\, v_i\right) dP_m$$

Now, x_i generally is constant at least in this particular example because the mass is not changing for any of the components and mass as there is no nuclear reaction kind of thing going on. So, you can assume mass to be in non-destructible or non-creatable. And therefore, x_i remains constant so taking that out. We can write this one now as:

$$\sum_{i=1}^{k} x_i\,(dh_i - T_m\, ds_i - v_i\, dP_m) = 0$$

again, as x_i is not changing so we can write:

$$dh_i = T_m\, ds_i - v_i\, dP_m$$

So, this gives us a way of estimating the change in enthalpy for the i^{th} component by estimating the changes entropy and change in pressure. So that if we somehow can calculate by knowing the property is the change in enthalpy and entropy, that problem will help us to calculate the change in the final pressure. For now, how to get the values for each of the components? For each of the component we have to get the reduced properties T_R and P_R, but initial state and also the final state and then from there we can compute the values of this T_m and P_m, quite similar to the Amagat's law approach. If V_m and T_m are given, then using that V_m we have to calculate an approximate value of P_m using ideal gas equation of state. And then putting it here we can get the value of T_m and P_m. Let me show you want numerical example which may make this particular concept clearer.

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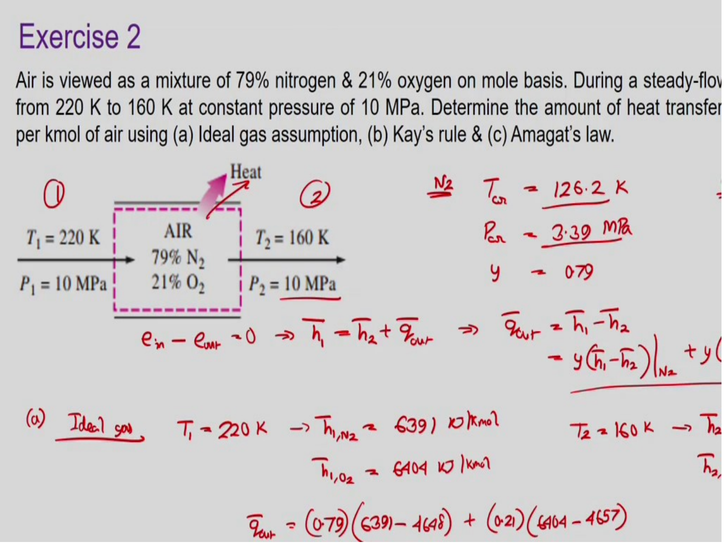

Exercise 2

Air is viewed as a mixture of 79% nitrogen & 21% oxygen on mole basis. During a steady-flo
from 220 K to 160 K at constant pressure of 10 MPa. Determine the amount of heat transfe
per kmol of air using (a) Ideal gas assumption, (b) Kay's rule & (c) Amagat's law.

N_2 $T_{cr} = 126.2$ K

$P_{cr} = 3.39$ MPa

$y = 0.79$

$$e_{in} - e_{out} = 0 \Rightarrow \bar{h}_1 = \bar{h}_2 + \bar{q}_{out} \Rightarrow \bar{q}_{out} = \bar{h}_1 - \bar{h}_2$$

$$= y(\bar{h}_1 - \bar{h}_2)\big|_{N_2} + y($$

(a) Ideal gas, $T_1 = 220$ K $\rightarrow \bar{h}_{1,N_2} = 6391$ kJ/kmol

$\bar{h}_{1,O_2} = 6404$ kJ/kmol

$T_2 = 160$ K $\rightarrow \bar{h}_2$

$\bar{h}_{2,}$

$$\bar{q}_{out} = (0.79)(6391 - 4648) + (0.21)(6404 - 4657)$$

Here the situation is, we are treating with air which can be viewed as a mixture of 79% nitrogen and 21% oxygen on mole basis. So here we can write, say,

$$y_{N2} = 0.79$$

$$y_{O2} = 0.21$$

This is a steady flow process so air is cooled from 220 K to 160 K at constant pressure of 10 MPa. So, pressure remains constant temperature changes from 220 K to 160 K. See the temperature is too small for these two gases to be considered as ideal gases. Because you are talking about particularly the end temperature as 160 K which is very small, quite close to the boiling point of oxygen. Then therefore we cannot consider or cannot assume either of the gases to be ideal gases for this particular combination of temperature and pressure, the pressure is also much higher. So, we have to now determine the amount of heat transfer during the process per kilo mole of air using the ideal gas approximation case rule and also Amagat's rule. So, we need to know the critical point values for nitrogen, I have noted the numbers:

$T_{cr} = 126.2$ K

$P_{cr} = 3.39$ MPa

For oxygen,

$T_{cr} = 154.8$ K

See final temperature is 160 K, it is just about 5 K higher than the boiling point of oxygen. And

P_{cr} for oxygen is 5.08 MPa.

So, the working pressure is also much higher and no way we can assuming the any of the gases to be ideal gas in this scenario. And let me just put it here in this case,

y for nitrogen = 0.79

and

y for oxygen = 0.21

So, let us go by the ideal gas approximation first. But during this particular process, this being a steady flow process so we can easily write that the energy coming in minus energy going out as to be equal to zero, i.e.,

$$e_{in} - e_{out} = 0$$

that is neglecting the changes in kinetic and potential energies and also assuming mass to be remaining constant. So, we can write that the state number 1, let us be the state 1 and this is state 2. Then,

$$\bar{h}_1 = \bar{h}_2 + \bar{q}_{out}$$

where

$h_{1\ bar}$ is the amount of energy coming in per unit mole of air

$h_{2\ bar}$ is the amount of energy going out per unit mole of air

q_{out} is the amount of heat rejected per unit mole

or

$$\bar{q}_{out} = \bar{h}_1 - \bar{h}_2$$

We do not yet know $h_{1\ bar}$ or $h_{2\ bar}$, which one is higher, if this quantity comes to a positive then, we can say that the direction we have assumed to be correct, that is heat is being rejected. If h_1 is lesser than h_2 then heat is being absorbed by the system.

Now $h_{1\ bar}$ and $h_{2\ bar}$ for molar sense, how we can write this? We can break this to two components. So, we can write:

$$= y(\bar{h}_1 - \bar{h}_2)|_{N_2} + y(\bar{h}_1 - \bar{h}_2)|_{O_2}$$

And now we have to identify this $h_{1\ bar}$ and $h_{2\ bar}$ for both the components, first using the ideal gas equation.

Using ideal gas equation, we know that given temperature

$T_1 = 220$ K

then we can either use ideal gas equation of state or we can directly take the values from the tables. Here we are going to take the values directly from the tables. So

$$\bar{h}_{1,N2} = 6391\ kJ/kmol$$

In any thermodynamic book you will find in appendix several deductibles are given, I have taken the value here from the book of Cengel and Boles.

So,

$h_{1\ bar}$ for oxygen = 6404 kJ/kmol

T_2 = 160 K

So, corresponding to 160 K,

$h_{2\ bar}$ for nitrogen = 4648 kJ/kmol

and

$h_{2\ bar}$ for oxygen = 4657 kJ/kmol

so, we know the values of enthalpies and we can done directly put it there now. Then amount of heat rejection per unit mole of the mixture or of air should be equal to:

$$\bar{q}_{out} = (0.79)(6391 - 4648) + (0.21)(6404 - 4657) = 1744\ kJ/kmol\ of\ air$$

The value is coming to be positive that means our assumed direction is correct. Heat is being rejected by the system. So that is for the ideal gas part, now we have to apply the Kay's rule that is when we are going to treat the it as a real gas.

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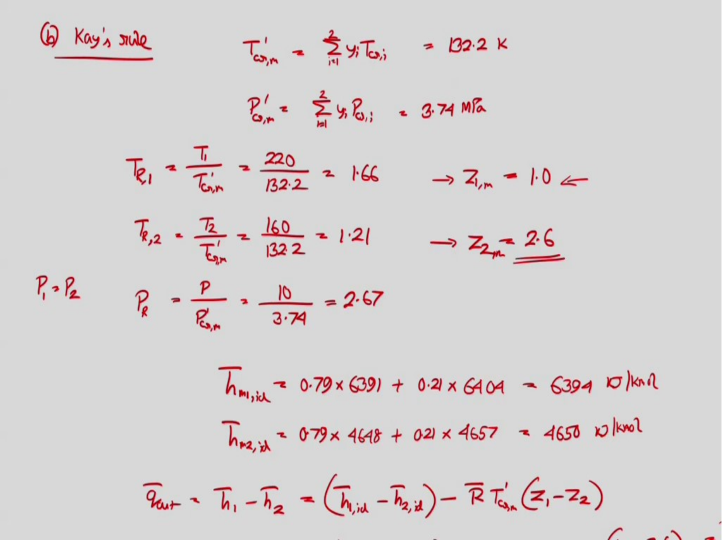

(b) Kay's rule

$$T'_{cr,m} = \sum_{i=1}^{2} y_i T_{cr,i} = 132.2\ K$$

$$P'_{cr,m} = \sum_{i=1}^{2} y_i P_{cr,i} = 3.74\ MPa$$

$$T_{R,1} = \frac{T_1}{T'_{cr,m}} = \frac{220}{132.2} = 1.66 \rightarrow Z_{1,m} = 1.0 \leftarrow$$

$$T_{R,2} = \frac{T_2}{T'_{cr,m}} = \frac{160}{132.2} = 1.21 \rightarrow Z_{2,m} = \underline{\underline{2.6}}$$

$P_1 = P_2$

$$P_R = \frac{P}{P'_{cr,m}} = \frac{10}{3.74} = 2.67$$

$$\bar{h}_{m1,id} = 0.79 \times 6391 + 0.21 \times 6404 = 6394\ kJ/kmol$$

$$\bar{h}_{m2,id} = 0.79 \times 4648 + 0.21 \times 4657 = 4650\ kJ/kmol$$

$$\bar{q}_{out} = \bar{h}_1 - \bar{h}_2 = (\bar{h}_{1,id} - \bar{h}_{2,id}) - \bar{R}T'_{cr,m}(Z_1 - Z_2)$$

To apply the Kay's rule, do you remember the Kay's rule that we have studied in the previous lecture? I hope you do so just apply that. To get the Kay's rule, we have to identify the pseudo critical temperature for the mixture. How we can do this? This will be equal to:

$$T'_{cr,m} = \sum_{i=1}^{2} y_i \, T_{cr,i} = 132.2\ K$$

So, in this case here I have already written the critical temperature for nitrogen and oxygen, also in their mole fraction. So, using the mole fractions, so can easily calculate this to be 132.2 K.

And similarly, the critical pressure for the mixture is:

$$P'_{cr,m} = \sum_{i=1}^{2} y_i \, P_{cr,i} = 3.74\ MPa$$

So, we have got the pseudo critical values for the mixture using their mole fractions. And now we have to identify the value of the compressibility factor for both the components. So, for that we need to know the reduce pressure at state number 1 which is:

$$T_{R,1} = \frac{T_1}{T'_{cr,m}} = \frac{220}{132.2} = 1.66$$

The reduced temperature at state 2 is:

$$T_{R,2} = \frac{T_2}{T'_{cr,m}} = \frac{160}{132.2} = 1.21$$

Reduced pressure for both state 1 and 2, because pressure remains constant, i.e., 10 MPa which is:

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

which is an isobaric process. So, P_1 and P_2 both are equal to each other, which is coming to be:

$$= \frac{10}{3.74} = 2.67$$

be very careful about the unit which you are using here. Everything is given MPa, so I do not have any issue. Otherwise I had to convert this. So, it is coming to be equal to 2.67. So, using this T_{r1} and T_{r2} you have to calculate the compressibility factor which is coming in this case to be quite close to 1. And Z_2 using P_r and T_{r2}, Z_1 for the mixture is 1.0 and Z_2 for the mixture is coming to be 2.6.

Now we have to calculate this particular thing for the mixture. How can we calculate this? Assume ideal gases, so initial enthalpy for this component should be equal to:

$$\bar{h}_{m\,1,ideal} = 0.79 \times 6391 + 0.21 \times 6404 = 6394\ kJ/kmol$$

$$\bar{h}_{m2,ideal} = 0.79 \times 4648 + 0.21 \times 4657 = 4650\ kJ/kmol$$

So now,

$$\bar{q}_{out} = \bar{h}_1 - \bar{h}_2 = (\bar{h}_{1,ideal} - \bar{h}_{2,ideal}) - \bar{R}T'_{cr,m}(z_1 - z_2)$$

the second term in the equation corresponds to the deviation because of the non-ideal gas behaviour or ideal gas behaviour.

Now we have just got these values:

$$= (6394 - 4650) - 8.314 \times 132.2(1 - 2.6) = 3503\ kJ/kmol\ of\ air$$

So, when we assume ideal gas our calculated number of 1744 whereas in this case the calculate value is much larger almost double of that.

So, and as we can estimate from these values at least from exit value it is far away from the critical point, whereas the first one is quite close, this is equal to 1 we can almost assume the ideal gas behaviour but definitely we can't do for the second situation. And for the Amagat's rule I am leaving it to you. Just try using the Amagat's law like in the previous lecture we have solved 1 problem of calculating the pressure and temperature using Amagat's law. Once we have that easily, we can get the corresponding enthalpy values also. Using the Amagat's law the results will be coming as 3717 kJ/kmol of air, which is a quite close to that one that we have calculated here. Try and see whether you can get this number or not. So, this way we can calculate most of the common intensive and extensive properties for a gas mixture, for both ideal gas and real gases.

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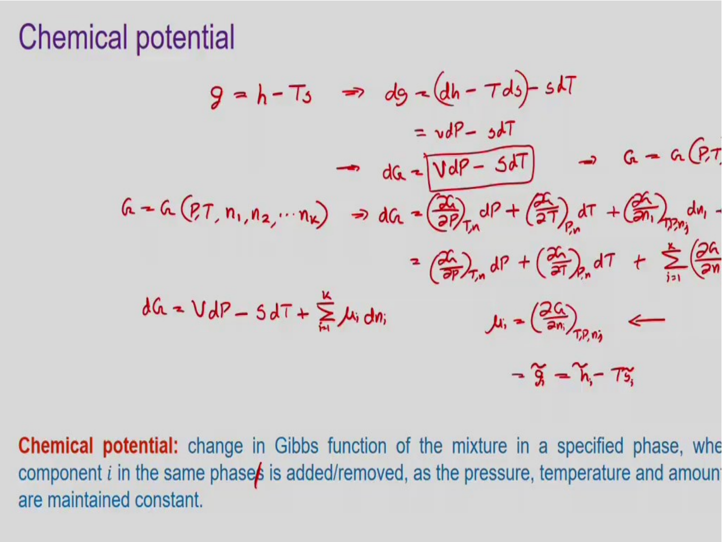

Chemical potential

$$g = h - Ts \Rightarrow dg = (dh - Tds) - sdT$$

$$= vdP - sdT$$

$$\rightarrow dG = \boxed{VdP - SdT} \rightarrow G = G(P, T$$

$$G = G(P, T, n_1, n_2, \cdots n_k) \Rightarrow dG = \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_j} dn_1 -$$

$$= \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \sum_{i=1}^{k} \left(\frac{\partial G}{\partial n\right.$$

$$dG = VdP - SdT + \sum_{i=1}^{k} \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \leftarrow$$

$$\rightarrow \tilde{g}_i = \tilde{h}_i - T\tilde{s}_i$$

Chemical potential: change in Gibbs function of the mixture in a specified phase, whe component *i* in the same phase~~s~~ is added/removed, as the pressure, temperature and amoun are maintained constant.

One final concept that I would like to introduce here, is which is known as the chemical potential. Now, chemical potential refers to the creation of the mixture. When you create a mixture, like suppose from the previous example, you have taken a certain quantity of oxygen and certain quantity of nitrogen and you are mixing them together. These two are miscible with each other and therefore very easily it creates a mixture.

Similarly, if we take suppose, say water and ethyl alcohol and we mix them together. They both are liquids and their very much miscible each other so that also creates aa very perfect mixture. But can you separate them now? We cannot, at least we cannot separate them directly. We have to put some kind of energy because the separation process will not be spontaneous. We have to spend some kind of exergy to get the separation between the strong components, separation between nitrogen and oxygen from air, or separation of water and ethyl alcohol from this liquid solution. And therefore we can easily see that this mixing process is irreversible in nature. It is highly irreversible in nature and it can go only in one direction. To get the reverse direction done we have to spend some exergy for this.

And that is exactly where, in order to calculate how much of work that we need to separate this, this concept of chemical potential comes into picture. I shall be discussing this one only very briefly and leaving the rest part to you. This is actually slightly advanced level topic, if you are interested you can proceed further from following any standard textbook.

Now in week number 2, when we discussed about different thermodynamic potentials, I introduced something known as the Gibbs free energy. Do you remember the expression? Gibbs free energy was defined using a symbol g and it was defined as:

$$g = h - Ts$$

or

$$\mathrm{d}g = \mathrm{d}h - T\mathrm{d}s - s\mathrm{d}T$$

and if we combine this one with the other $T\mathrm{d}s$ relation, we can write this one as:

$$= v\mathrm{d}P - s\mathrm{d}T$$

because

$$\mathrm{d}h - T\mathrm{d}s = v\mathrm{d}P$$

from the second $T\mathrm{d}s$ relation. Or if we go to the extensive definition, we can write this as:

$$\mathrm{dG} = V\mathrm{d}P - S\mathrm{d}T$$

So, this was the definition of Gibbs free energy that was provided earlier. And as long as you are dealing with the pure substance, this is sufficient. For a pure substance, we can easily say that this *G*, this function of only pressure and temperature. However, when we are dealing with a mixture then this also because functions of all the compositions that is for a mixture G is a function of pressure, temperature and all the mole fractions.

$$G = f(P, T)$$

or I should say the number of moles for all the components if their k number of components. So that we can write:

$$G = \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_j} dn_1 + \ldots\ldots\ldots + \left(\frac{\partial G}{\partial n_k}\right)_{T,P,n_j} dn_k$$

Hence apart from this we have to the last one *nj dn_k* if where I do the summation form when we write this in the form:

$$= \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \sum_{i=1}^{k} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j_{j=1\to k, j\neq i}}} dn_i$$

with *T, P* and n_j remaining constant, dn_i, where *j* varies from 1 to *k*, but j is not equal to *i*. If we are talking about a pure substance or a single component substance then the third term is equal to zero.

So, this will be back to the pure substance equation. But when we are having the multi compound mixture then, of course the third term is also relevant. And if you now compare this one with the form for this pure substance then probably, we can get a unified form as:

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + \sum_{i=k}^{k} \mu_i \, dn_i$$

where

$$\mu_i = \left(\frac{\partial G}{\partial n_k}\right)_{T,P,n_j}$$

This is called the chemical potential that I am talking about. So, this chemical potential represents the changes in Gibbs function of the mixture in a specified phase, when a unit amount of component *i* in the same phase is added or removed from the mixture, as the pressure temperature and amount of all other phases are maintained constant. Quite often we also represent this one by something like:

$$\tilde{g}_i = \tilde{h}_i - T\tilde{s}_i$$

Here these are for the i^{th} component, and these quantities *g tilde*, *h tilde*, *s tilde* are also called the partial molar properties for the mixture or for the i^{th} component in the mixture.

So, this μ_i is the chemical potential that comes into picture, whenever we are talking about a multicomponent mixture. Now, you probably have observed several situations when we mix two components whatever we expect that does not happen. Like suppose you have mixed a certain quantity of, say, 200 ml of water and 100 ml of ethyl alcohol. And then what you have mixed, you can expect the final volume of the mixture to be equal to 300 ml, but that does not happen. Generate the final volume is slightly less than this or sometimes when we mix two substances together, there is a change in temperature, either the temperature reduces or the temperature increases. And that happens because of the presence of this chemical potential.

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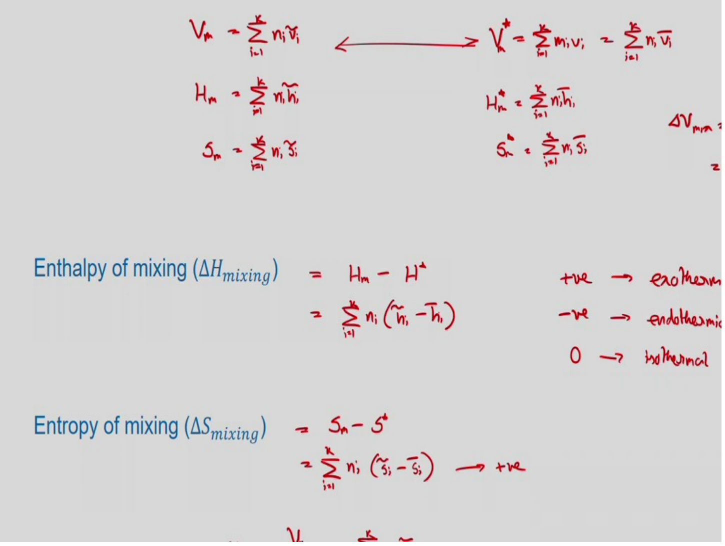

$$V_m = \sum_{i=1}^{k} n_i \tilde{v}_i \longleftrightarrow V_m^* = \sum_{i=1}^{k} m_i v_i = \sum_{i=1}^{k} n_i \bar{v}_i$$

$$H_m = \sum_{i=1}^{k} n_i \tilde{h}_i \qquad H_m^* = \sum_{i=1}^{k} n_i \bar{h}_i$$

$$S_m = \sum_{i=1}^{k} n_i \tilde{s}_i \qquad S_m^* = \sum_{i=1}^{k} n_i \bar{s}_i$$

$\Delta V_{mix} =$

$=$

Enthalpy of mixing (ΔH_{mixing}) $= H_m - H^*$

$= \sum_{i=1}^{k} n_i (\tilde{h}_i - \bar{h}_i)$

+ve → exotherm

−ve → endothermi

0 → isothermal

Entropy of mixing (ΔS_{mixing}) $= S_m - S^*$

$= \sum_{i=1}^{k} n_i (\tilde{s}_i - \bar{s}_i)$ → +ve

So, once we want to calculate the final volume for the mixture, then we can expect this final volume to be equal to:

$$V_m{}^* = \sum_{i=1}^{k} m_i v_i$$

if we write this in molar sense maybe we can also write this one as:

$$= \sum_{i=1}^{k} n_i \overline{v_i}$$

But practically it does not happen for several very common kind of scenarios. Therefore, let us denote this one as V*.

Practically,

$$V_m = \sum_{i=1}^{k} n_i \tilde{v}_i$$

where

v$_i$ tilde is the partial molar specific volume that we have just defined.

Similarly,

$$H_m = \sum_{i=1}^{k} n_i \tilde{h}_i$$

where we defined a starred quantity as:

$$H_m{}^* = \sum_{i=1}^{k} n_i \overline{h}_i$$

and we can define the entropy for the mixture as:

$$S_m = \sum_{i=1}^{k} n_i \tilde{s}_i$$

And where *S$_m$**represents:

$$S_m{}^* = \sum_{i=1}^{k} n_i \overline{s}_i$$

these two quantities are not equal. only if you are talking about an ideal gas mixture then these two quantities are equal. But for real situations there not at all equal to each other. And therefore, there is a deviation between the two. If we consider this deviation, we can define:

$$\Delta V_{m,n} = V_n - V^*$$

$$= \sum_{i=1}^{k} n_i \left(\tilde{v}_i - \overline{v}_i\right)$$

Similarly, we can define an enthalpy of mixing, *ΔH$_{mixing}$* which is nothing but:

$$\Delta H_{mixing} = H_m - H^*$$

$$= \sum_{i=1}^{k} n_i \left(\tilde{h}_i - \overline{h}_i\right)$$

and the entropy of mixing the same way,

$$\Delta S_{mixing} = S_m - S^*$$

$$= \sum_{i=1}^{k} n_i \left(\tilde{s}_i - \overline{s_i}\right)$$

Now, mixing process being an irreversible one, so entropy of mixing is always positive. Entropy of mixing is always positive therefore; entropy of the mixture is always higher than the summation of the mixture components or before the mixing process taken place. Whereas enthalpy of mixing can be positive, can be negative, can be zero also in special cases. When it is positive then heat is being produced, we call that reaction to be exothermic or that mixing process are called to be exothermic. Whereas when it is negative, we call that mixing process to be endothermic and when that is zero, then we call the mixing process to be isothermal. In an isothermal mixing, during the process there will be no change in temperature. During exothermic and endothermic mixings, there is a change in temperature of the final mixture compared to the initial temperatures. So quite often we may have to define specific versions of these quantities also. Like if we want to define the specific volume of this mixture then that should be:

$$v_m = \frac{V_m}{n} = \sum_{i=1}^{k} y_i \, \tilde{v}_i$$

Similarly, specific enthalpy of the mixture:

$$h_m = \frac{H_m}{n} = \sum_{i=1}^{k} y_i \, \tilde{h}_i$$

And for specific entropy of the mixture:

$$s_m = \frac{S_m}{n} = \sum_{i=1}^{k} y_i \, \tilde{s}_i$$

So, this why we can calculate the values for the mixture taking into the taking this chemical potential into account. I am not going any further in this chemical potential, but by using this concept it is possible to calculate the work requirement for the separation. I am leaving that to anyone who is interested to learn, because that is more and advanced thermodynamic kind of concept. That is where I would like to finish this particular week.

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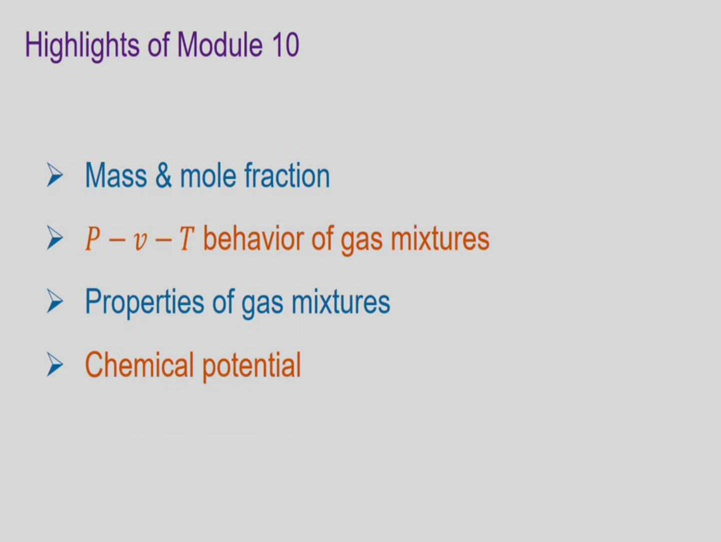

Highlights of Module 10

- Mass & mole fraction
- $P - v - T$ behavior of gas mixtures
- Properties of gas mixtures
- Chemical potential

Here, we have learnt about the mass and mole fraction, the P - v - T behaviour of gas mixtures both ideal and real gas mixtures, then the properties of gas mixtures we have discussed today and finally a very brief introduction to the chemical potential. There are several other concepts that could have been discussed in conjunction with gas mixtures, but I do not want to go any for that because that is not relevant to this course as well.

As I just told that can be the topics of advanced thermodynamics, which is beyond the scope of this particular course. So that is where our week number 10 finishes. In the next week I shall be starting with another kind of mixture, where we shall be talking about the mixing of ideal gas and or I should say a non condensable gas and condensable vapour which has its application in the field of air conditioning. Till then you rehearse this lecture and if you have any queries, please write back to me. Thank you.