Engineering Thermodynamics
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Lecture – 46
Properties of Ideal Gas Mixtures: Equation of state. Conservation equations

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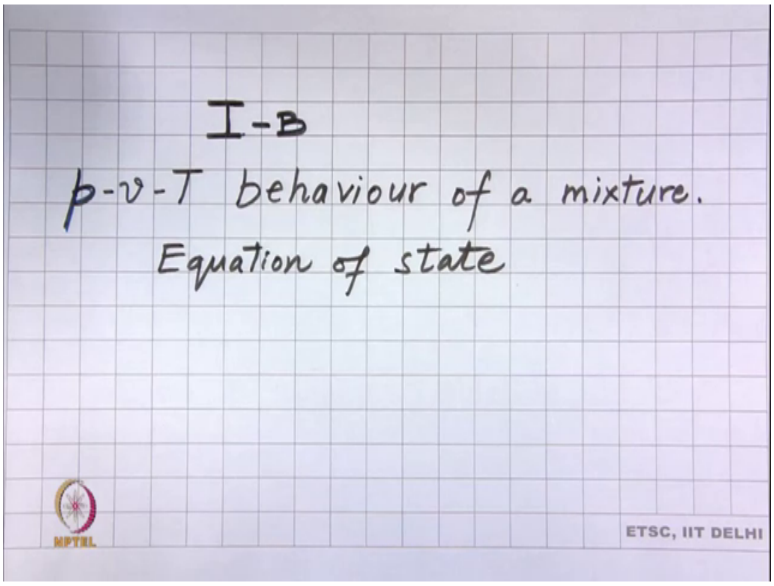

I-B

p-v-T behaviour of a mixture.

Equation of state

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This is the second lecture of the mixture properties. In the first part, we develop relations for the basic properties of a mixture, like its mass, specific volume, density, and mixture molar mass. We will now extend that to say how can we is that enough to get the p-v-T behavior of a mixture.

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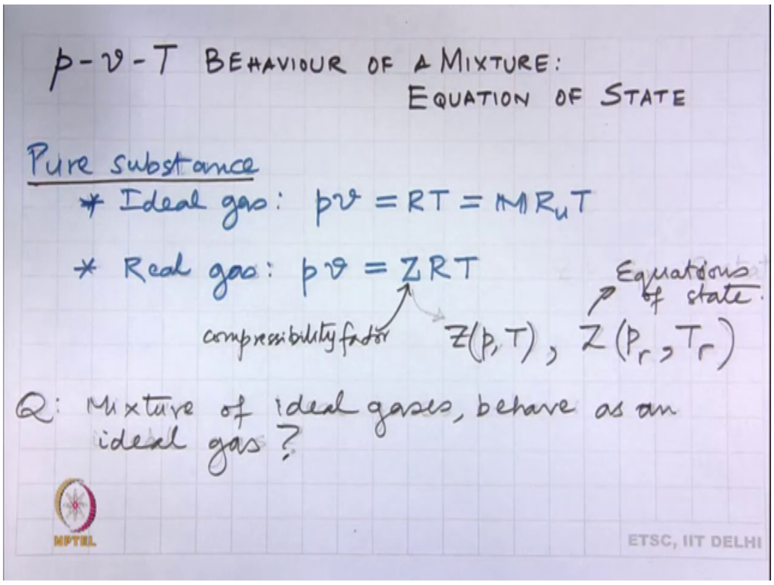

p-v-T BEHAVIOUR OF A MIXTURE:
EQUATION OF STATE

Pure substance

- Ideal gas: $pv = RT = MR_uT$
- Real gas: $pv = ZRT$

compressibility factor $\rightarrow Z(p,T)$, $Z(p_r, T_r) \leftarrow$ Equations of state

Q: Mixture of ideal gases, behave as an ideal gas?

So, we go back to what we have already learned that for a pure substance, where the ideal gas equation of state, where we said p v is equal to R T or in terms of the molar mass and the universal gas constant that is what it is. For a real gas, we modified this equation p v is equal to Z R T, where Z is the compressibility factor.

And if you recall from single phase thermodynamics, Z depends on the state the pressure and temperature, in particular we got the tables in terms of reduced pressure and reduced temperature by dividing these by the respective critical values. And from there, we developed different types of equations of state. Like Van der Waals equation of state, BT Bridgeman equation of state, and so many others, so that was good enough for this part, where we were looking at the pure substance.

And now we say that if I have a mixture of two ideal gases or three ideal gases, thus this mixture behave like an ideal gas, so that is the question. There is a mixture of ideal gases, behave as an ideal gas. The implications of this are very far reaching. If the answer is yes, then we can use the same relations that we had for a pure substance, life becomes very easy, the calculations are very straight forward.

If the answer is no, we are to going to much more involved calculations to get an answer. And there to, it will come only at the expense of sacrificing some of the accuracy, was very accurate solutions, we will have to going to much deeper behavior of individual species use much more complex models, and get much more accurate answers that is not within the scope of this particular course.

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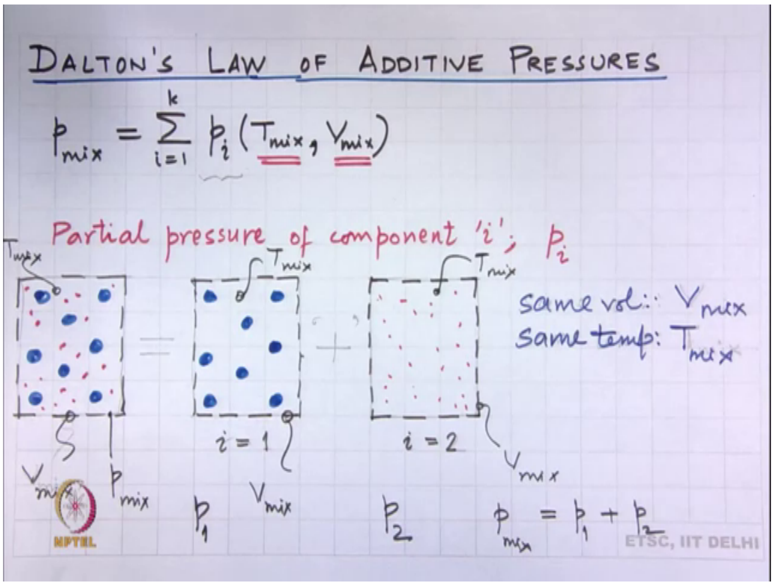

So, to do that we invoke use two laws, and they help us in going forward in answering that question. First is Dalton's law of additive pressures, the second one we will look at is Amagat's law of additive volumes. So, this law is somewhat familiar from school days, but Dalton's law partial pressures has been taught with such that the mixture pressure with the sum of the pressure of the individual components.

Now, we will make it more rigorous by saying that mixture pressure is pressure exerted by the individual components provided, the individual component were at the same temperature as the mixture temperature and that component occupy with the same volume as the mixture volume, so that is the difference that we are now looking at. So, here is what it means that if this is the system, and here we have one species which is the blue dots, and the second species which is the red dots. This system its volume is V mix, and the pressure that you would measure here is p mix, and this system is at a temperature of T mix.

And now what we are saying in Dalton's law of additive pressures is that if I take the same system, and now I only place one type of this molecules in this, say this blue ones. In which cases, the blue ones is species number 1, and because it is the same volume that we are taken here, this is V mix same as this one. And we keep this at the same temperature T mix as the mixture temperature. Under this situation, the pressure exerted by this species is p 1 in this case a i equal to 1.

And now we say it was a binary mixture, this was i 1. Then we do the same thing with the second component of their mixture, and now we are saying this is i is equal to 2. And now we are only looking at the other species which is the red dots over there, and we maintain the same conditions that this volume is V mix, its temperature same as the mixture temperature T mix, then the pressure exerted by this second species in this case is p 2. And then p mix is equal to p 1 plus p 2.

So, what we have done to what we have already learned in school is added condition that partial pressure is the pressure exerted by the species, if it were to occupy by itself. The same volume as that of the mixture, and b at the same temperature as that of the mixture. So, these are very important considerations same volume V mix and same temperature T mix, so that is Dalton's law of additive pressures.

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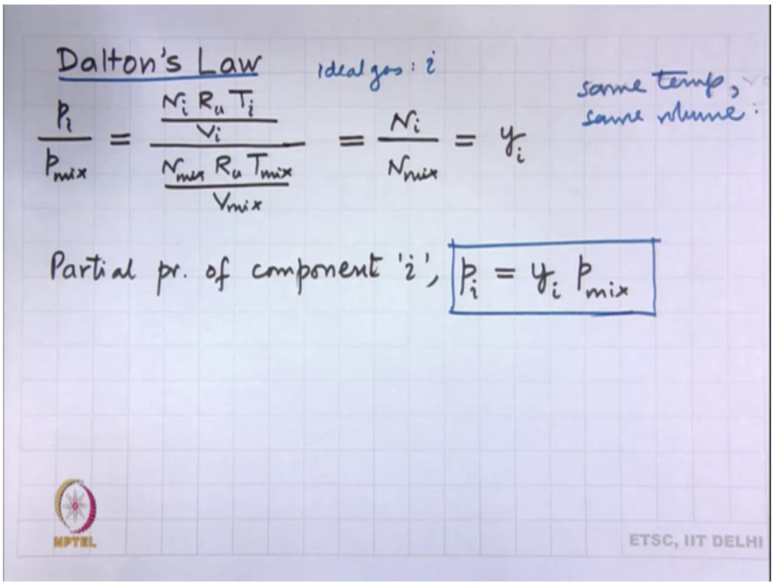

Dalton's Law

ideal gas : i

same temp, same volume

$$\frac{p_i}{p_{mix}} = \frac{\frac{N_i R_u T_i}{V_i}}{\frac{N_{mix} R_u T_{mix}}{V_{mix}}} = \frac{N_i}{N_{mix}} = y_i$$

Partial pr. of component 'i', $\boxed{p_i = y_i \, p_{mix}}$

A consequence of this law is that we can now extend it, and say that I will now look at the ratio of the partial pressure of ith component, this is the partial pressure of the component i to the mixture pressure. And this we can write that ith component is an ideal gas, so p i is N i R u T i by V i. And we write the same thing for the mixture N mix R u T mix upon V mix, we simplifying it, this becomes number of moles of i divided by mixture moles which is nothing but what we just defined as y i, which is the molar fraction of the ith component.

And this we are of course as before, we are doing at the same temperature, same volume. So, we can say that the partial pressure of component i is p i which is equal to its molar fraction multiplied by the mixture pressures. So, this is another important relation came about because of Dalton’s law.

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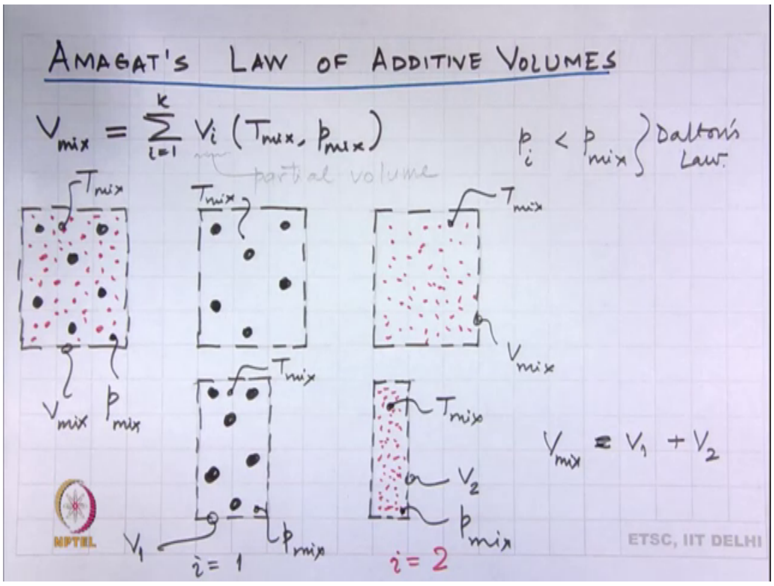

We now go to the second law, which is Amagat’s law of additive volumes. Simply put it says that V mix is the summation of V i provided the component occupy is at the same temperature, and the same pressure as the mixture. So, here is what it means that is this is the system. And we have two components there, one is this one, and the others are here.

Then if we separate it, the way we did few minutes back look by looking at Dalton’s law, we would get the same type of the situation. So, we are saying that now I only have this, but now the pressure of the ith component is less than the mixture pressure, so that is what came about there the p i is less than p mix, when you do this separation, and that came from Dalton’s law.

But Amagat’s law requires that the volume of the mixture will be volume occupied by this species, it were at the same temperature as the mixture. So, we have this mixture was at T mix, and the volume of this was V mix, and the pressure inside here was p mix.

When we separated out the volume was the same, we could have maintain the same temperature, but pressure will always be less than the mixture pressure.

And this is what Amagat's law says that if you were now to maintain the same temperature T mix, and maintain the same pressure p mix, then the volume that this species would occupy, if I did for all the species will equal to the volume of the mixture, which means that this particular case, we would have to increase its pressure, so that this becomes T mix, its pressure now becomes T mix, but this volume has now come down, so volume of this is now V 1. So, this was i equal to 1. So, the volume occupied by the ith component, if it were at the same temperature and pressure as the mixture temperature.

Now, we do the same thing for the second component, so that is the same volume as the earlier case, this we are saying this is V mix. But, now we only have, i equal to 2 the second component of the mixture in this, so which is nothing but all these molecules here. Now, we know that even if you were to attain T mix, then the pressure here again will be its partial pressure of this component which will be less than the mixture pressure, but Amagat's law requires that this component should also be at this same pressure as the mixture volume, mixture pressure, and the same temperature as the mixture temperature.

For that again, we will have to reduce the volume of this one. So, all this is now this molecules are now, you know smaller volume such that the temperature is the same as the mixture temperature. The volume is now V 2, and the pressure is the mixture pressure. And what Amagat's law says that in this condition V mixture is V 1 plus V 2. And if we add more mixtures, we did the same thing with each one of them, it will be the relation that we have right here V mix is the sum of the volumes of the individual species, if they were to occupy a volume at the same temperature and pressure was that of the mixture. So, this is Amagat's law of additive volumes.

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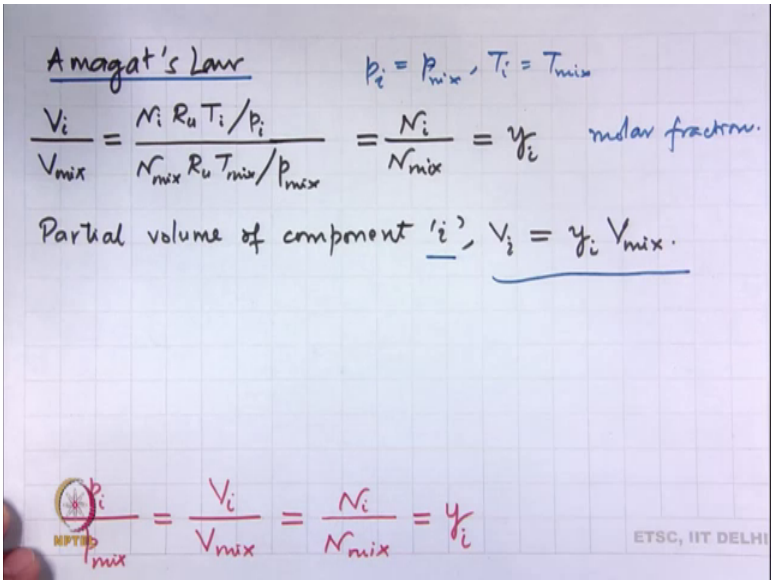

Amagat's Law

$p_i = p_{mix}$, $T_i = T_{mix}$

$$\frac{V_i}{V_{mix}} = \frac{N_i R_u T_i / p_i}{N_{mix} R_u T_{mix} / p_{mix}} = \frac{N_i}{N_{mix}} = y_i$$

molar fraction.

Partial volume of component 'i', $V_i = y_i V_{mix}$.

$$\frac{p_i}{p_{mix}} = \frac{V_i}{V_{mix}} = \frac{N_i}{N_{mix}} = y_i$$

So, we now have two ways of connecting various properties of components and to the mixture. So, we extend Amagat's law like we did with Dalton's law V i by V max V mix mixture is N i R u T i by p i which is and volume of the mixture is N mix R u T mix upon p mix recall that in this case, we are keeping the same temperature and the same pressure. So, all the p i's are equal to p mix, and T i equal to T mix in which case V i by V mix becomes N i by N mix which is nothing but small y i the molar fraction.

So, what is now we called by Amagat's law. These are the partial volume of component i, V i is equal to the molar fraction of i multiplied by the mixture volume. So, what has emerged from this set of definitions with that p i by p mix is equal to V i by V mix is equal to N i by N mix which is the molar fraction. So, this is something that comes out from both the laws.

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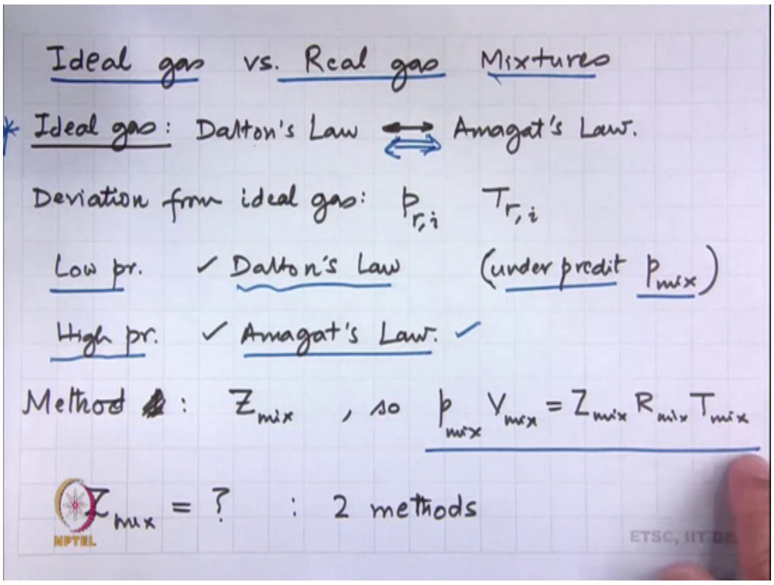

Ideal gas vs. Real gas Mixtures

* Ideal gas : Dalton's Law $\rightleftarrows$ Amagat's Law.

Deviation from ideal gas: $p_{r,i}$ $T_{r,i}$

Low pr. ✓ Dalton's Law (under predit p_{mix})

High pr. ✓ Amagat's Law. ✓

Method [illegible] : Z_{mix} , so $p_{mix} V_{mix} = Z_{mix} R_{mix} T_{mix}$

Z_{mix} = ? : 2 methods

So, can we apply both laws to all situations well so happens that, when we look at ideal gases, and real gas mixtures. So, we have for an ideal gas Dalton's law is equivalent to Amagat's law. So, what we would predict using Dalton's law is the same as what we would predict using Amagat's law, and that is strictly for an ideal gas.

So, what happens is that for low pressures Dalton's law is better and predicting the behavior, but at high pressures Amagat's law is better. And the reason is that Dalton's law does not take into account the fact that when we were mixing two molecules, intermolecular forces are not being taken care off. To some extent that is taken care of by Amagat's law, because there the volumes are being kept, so the intermolecular interactions are somewhat accounted for. And so at high pressures Amagat's law is better, at low pressures Dalton's law is better. But, Dalton's law at high pressures, under predicts the mixture pressure, so that is one thing that comes out ok.

Now, we want to say now we will take the steps further, and say now I want the p-v-T relationship for a mixture or in some sense an ideal gas equation of state for a mixture or a modification of that with the compressibility factor. So, we are now looking for is an expression, where we are looking for something like this, and asking how good is this p mix, V mix is equal to Z mix R mix into T mix.

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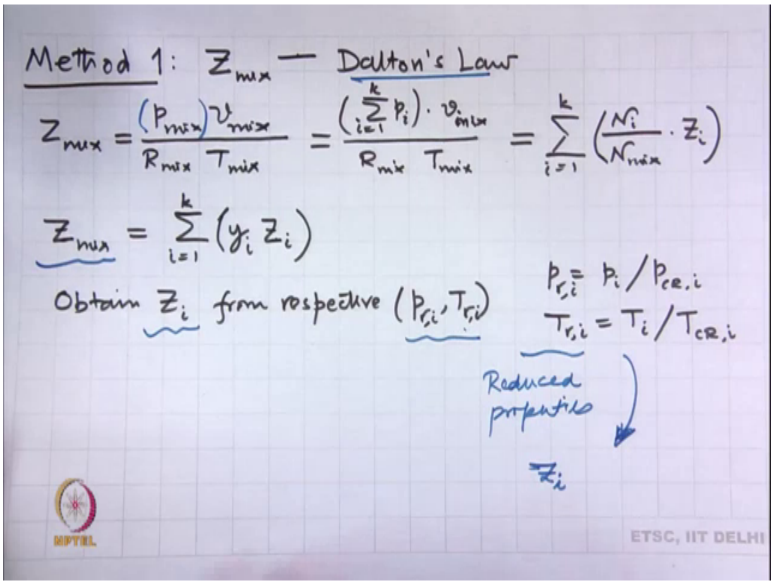

Method 1: Z_{mix} — Dalton's Law

$$Z_{mix} = \frac{(p_{mix})v_{mix}}{R_{mix}\ T_{mix}} = \frac{\left(\sum_{i=1}^{k} p_i\right) \cdot v_{mix}}{R_{mix}\ T_{mix}} = \sum_{i=1}^{k}\left(\frac{N_i}{N_{mix}} \cdot Z_i\right)$$

$$Z_{mix} = \sum_{i=1}^{k}(y_i Z_i)$$

Obtain Z_i from respective $(p_{r,i}, T_{r,i})$

$p_{r,i} = p_i / p_{cr,i}$

$T_{r,i} = T_i / T_{cr,i}$

Reduced properties

Z_i

So, we have two methods for tackling this problem. Method one is that we predict the compressibility factor for the mixture by Dalton's law. So, what we do here is that we define Z mix as p mix v mix upon R mix T mix equal to and then we say that the mixture pressures by Dalton's law is a sum of the partial pressures of each component. And by putting that we get this relation that this is summation of N by N i by N mix multiplied by Z i. So, what remains here is the compressibility factor for the ith component.

And so it gives a very elegant relation that the mixture compressibility factor is the summation of y i Z i is the molar fraction of i multiplied by the compressibility factor of ith component. Getting the ith component compressibility factor is something we have already learned in part one of thermodynamics that we need the reduced pressures for that component, and the reduced temperature for that component, where these are defined as p i upon critical pressure and temperature upon critical temperature. So, these are the reduced properties.

So, we got the reduced properties from the reduced properties, we go to the generalized compressibility chart or many of the other equations that we have. And using that we got Z i. And if we know the molar composition of the mixture, we can then combine this with that to get the compressibility factor for the mixture. And then we can go back toward equation of state with this particular value of Z mix, so that completes the calculation.

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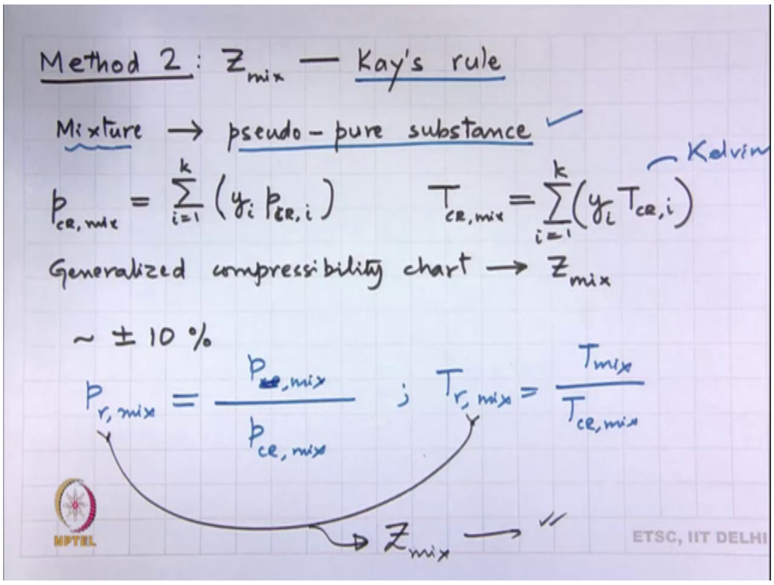

Method 2 : Z_{mix} — Kay's rule

Mixture → pseudo-pure substance ✓

$p_{cr,mix} = \sum_{i=1}^{k} (y_i \, p_{cr,i})$ $T_{cr,mix} = \sum_{i=1}^{k} (y_i \, T_{cr,i})$ — Kelvin

Generalized compressibility chart → Z_{mix}

~ ± 10 %

$p_{r,mix} = \frac{p_{\cancel{cr},mix}}{p_{cr,mix}}$; $T_{r,mix} = \frac{T_{mix}}{T_{cr,mix}}$

→ Z_{mix} → //

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In the second method, we do something else which is we invoked what is called Kay's rule. And here this is the fundamental difference from the first method that we just saw in that we treat the mixture as a pseudo pure substance. What does it mean that we know that the mixture has got different molecules in it, but we are going to ignore that difference, and say this whole thing behaves like some sort of a homogeneous material and that is why we put the word a pseudo pure substance? So, we are assigning this mixture so called hypothetical single molecule, which is a quote unquote pure substance.

So, what we do in that case if that we then say that the critical pressure of the mixture is weighted by the molar fractions of the mixture multiplied by the critical pressure of the individual components. Same similarly that critical temperature of the mixture can be obtained by the weighted product of the molar fraction, and the critical temperature of the individual species, remember this is all in kelvin.

So, we got the critical pressure of the mixture critical temperature of the mixture from that we can get the reduced pressure of the mixture, this is p critical mixture sorry p mix p mixture divided by p critical mixture. And similarly, reduced temperature for the mixture will be T critical mixture upon this is T mixture in the numerator. Now, what we do is we take these values go to the generalized compressibility chart or some other relation, and get z mixture. And from there we can use that equation of state, and get all the other properties.

So, now what we have got, if the ability to be able to get more information about the properties based on Dalton's law, Amagat's law, and on Kay's rule. The next question we ask with that to solve a problem, we need internal energy, specific enthalpy, and specific entropy, how do we get those properties. Now, that we have any questions on state for us with the compressibility factor put in, we can get all the other relations in a straightforward manner.

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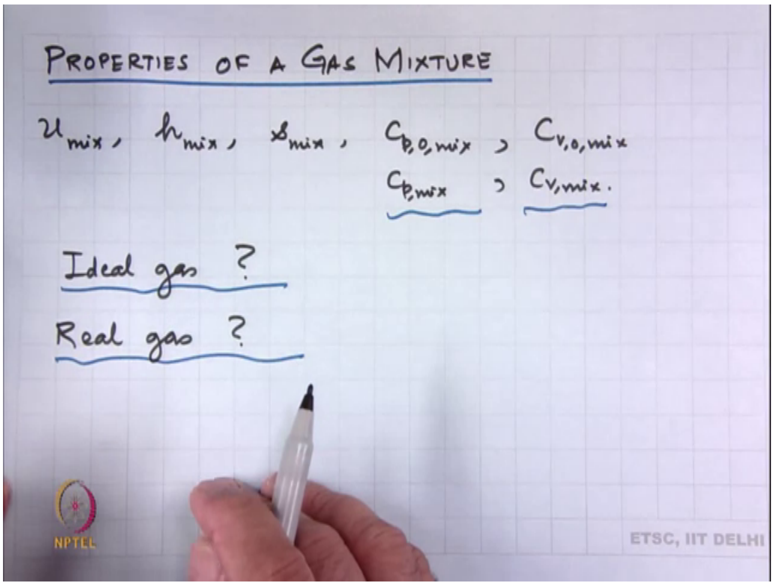

PROPERTIES OF A GAS MIXTURE

$u_{mix}, \ h_{mix}, \ s_{mix}, \ c_{p,0,mix}, \ c_{v,0,mix}$

$c_{p,mix}, \ c_{v,mix}.$

Ideal gas ?

Real gas ?

So, here is what we will be now look at is properties of a gas mixture. And what we want a specific internal energy of the mixture, specific enthalpy of the mixture, specific entropy of the mixture, constant pressure specific heat of the mixture, and constant volume specific heat of the mixture. So, we will first look at the Kay's which we have looking at ideal gases, and then for real gases.

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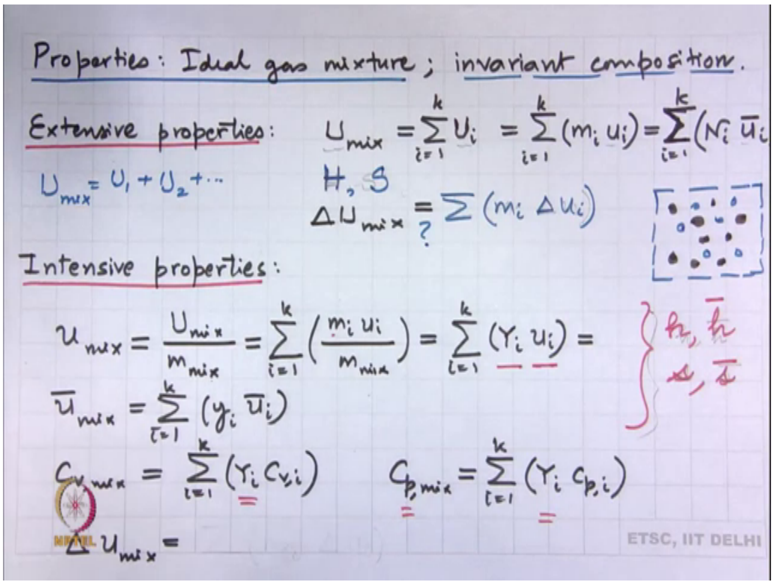

Properties: Ideal gas mixture ; invariant composition.

Extensive properties: $U_{mix} = \sum_{i=1}^{k} U_i = \sum_{i=1}^{k} (m_i u_i) = \sum_{i=1}^{k} (N_i \bar{u}_i$

$U_{mix} = U_1 + U_2 + \cdots$

H, S

$\Delta U_{mix} \underset{?}{=} \sum (m_i \Delta u_i)$

Intensive properties:

$$u_{mix} = \frac{U_{mix}}{m_{mix}} = \sum_{i=1}^{k} \left(\frac{m_i u_i}{m_{mix}} \right) = \sum_{i=1}^{k} (\underline{Y_i} \, \underline{u_i}) =$$

$$\left. \begin{matrix} h, \bar{h} \\ s, \bar{s} \end{matrix} \right\}$$

$$\bar{u}_{mix} = \sum_{i=1}^{k} (y_i \bar{u}_i)$$

$$c_{v,mix} = \sum_{i=1}^{k} (Y_i \underline{\underline{c_{v,i}}}) \qquad \underline{\underline{c_{p}}}_{mix} = \sum_{i=1}^{k} (\underline{\underline{Y_i}} \, c_{p,i})$$

$$\Delta u_{mix} =$$

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So, what happens is what we are saying is that the properties of a mixture of ideal gases, we are only looking at one particular state. And we are saying that at that particular state, there is no change in its composition. So, we say we have a system in which we have this mixture, there is one component there, and the second component there, and it could be more components there.

Then the first thing we do is, we will say the simple thing to tackle is the extensive properties of this mixture. And so we say that extensive properties are nothing but edition of the extensive properties of the individual components. So, U mix which is the total internal energy of the mixture is the sum of the internal energy of every component of that mixture, so that means this summation is basically telling you that U mix is equal to U 1 plus U 2 plus like that till k.

So, this is this helps us, because U 1 can be written as the mass of that particular component multiplied by its internal specific internal energy m i u i or in terms of moles N i u i bar, it is the molar specific internal energy. In the same way, we can write a substitute for U by H, and we get the enthalpy of the mixture. And you can substitute U by S, and get the total entropy of the mixture. Both these are nothing but sums of respective property contributed by every component in the mixture.

We can also then ask what is the change in the internal energy of the mixture, and we will write little more detailed things little later on. One could say that this is m i into delta u i, but this is a question mark on this, for reason we will come to that in a few minutes ok. So, we got one part of the property things done which is the extensive properties U, H, S being taken care of.

Now, we ask how do we get the intensive properties of a mixture. And that is where this first part helps us that the specific internal energy of the mixture is extensive plus the total energy of the mixture divided by the mixture mass, which is summation of everything in the numerator m i u i, and mix this being common this goes in the denominator. And simplifying it this becomes the product of the mass fraction, and the specific internal energy, so that is a very nice thing to have that U mix is equal to summation of Y i capital Y i into U i or Y i which is the molar ratio fraction multiplied the molar specific heat.

And one can do this thing, and get h, h bar, s and s bar. We can now extend this also to get the specific heats, the same way that we did earlier. So, C v of the mixture will come up to be summation of Y i C v i, Y is the mass fraction, and same thing with constant specific heat, we wait to a weighted sum of the product of the ith component specific heat and its mass fraction.

So, in this sense we got all the properties that we have been looking for, and what it is telling us is that if we know the mass fraction or the molar fraction of the component, and the specific property of the individual components. Then using these relations, we can compute the specific internal energy of the mixture. So, this is what we have accomplish now.

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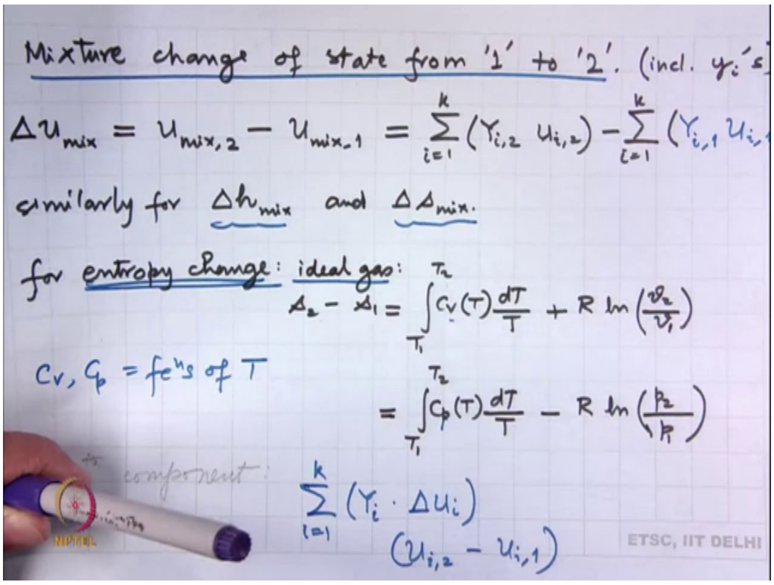

Mixture change of state from '1' to '2'. (incl. y_i's

$\Delta u_{mix} = u_{mix,2} - u_{mix,1} = \sum_{i=1}^{k}(Y_{i,2}\; u_{i,2}) - \sum_{i=1}^{k}(Y_{i,1}\; u_{i,}$

similarly for $\underset{\sim}{\Delta h_{mix}}$ and $\underset{\sim}{\Delta s_{mix}}$.

for entropy change: ideal gas:

$$s_2 - s_1 = \int_{T_1}^{T_2} c_v(T)\frac{dT}{T} + R\ln\left(\frac{v_2}{v_1}\right)$$

c_v, c_p = fc^n's of T

$$= \int_{T_1}^{T_2} c_p(T)\frac{dT}{T} - R\ln\left(\frac{p_2}{p_1}\right)$$

component:

$\sum_{i=1}^{k}(Y_i \cdot \Delta u_i)$

$(u_{i,2} - u_{i,1})$

We now ask what happens to changes of the mixture properties. So, you are asking this question that the mixture changes state from state 1 to state 2. And we are looking at the general case, where the states could be such that the system could be open, and that you could have added or subtracted some of the species, what happens in that case.

So, there we have that delta U of the mixture will be specific internal energy of the mixture in state 2 minus specific energy of the mixture in state 1, which is summation i at for state 1 for state 2 Y i 2 U i 2 product minus the same thing, but this time it will be Y i 1, U i 1 that total. So, what we have done here is that we have allowed for changes in the mass fractions or the molar fraction of any of the components of a mixture. If there was no change in the component mixture components, then this relation will become simpler, and it will just become summation i equal to 1 to k into say Y i which did not change during the process multiplied by delta U i which is nothing but U i 2 minus U i 1. And we can based on this get similar properties for changes in the enthalpy specific enthalpy, and specific entropy of the mixture.

But, little care has to be exercise, when will look at entropy change for an ideal gas. We have learned that entropy change of an ideal gas is s 2 minus s 1 which is integral T 1 to T 2 C v dT dT by T plus R ln V 2 by V 1 or in terms of pressure C p d T by T minus R l n p 2 by p 1. So, what we are seeing basically in both these relations that we learned in the first course that C v and C p are functions of temperature. We did not assume constant temperature, constant specific heats. Now, the same relation can be written for any ith component by adding the subscript i s i, 2 minus s i, 1 is equal to all of these things.

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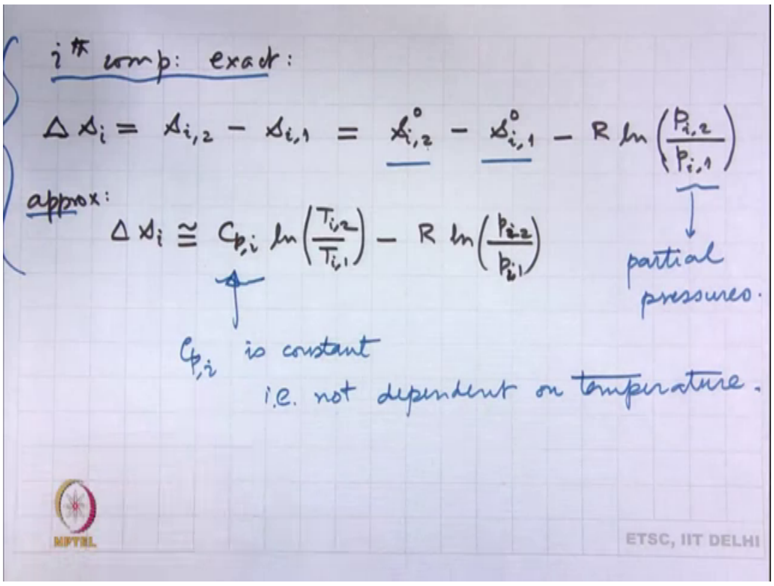

i^{th} comp: exact:

$$\Delta s_i = s_{i,2} - s_{i,1} = \underline{s^{\circ}_{i,2}} - \underline{s^{\circ}_{i,1}} - R \ln\left(\frac{p_{i,2}}{p_{i,1}}\right)$$

partial pressures.

approx:

$$\Delta s_i \cong c_{p,i} \ln\left(\frac{T_{i,2}}{T_{i,1}}\right) - R \ln\left(\frac{p_{i,2}}{p_{i,1}}\right)$$

$c_{p,i}$ is constant

i.e. not dependent on temperature.

So, now what happens is if you want the exact solution for the ith component, then delta s i is s i, 2 minus s i, 1 which is s, i 2 0 which is the standard state entropy minus s i, 1 0 minus R l n p i, 2 by p i 1. So, during the pressures became the partial pressures. And these are standard state entropy values. So, this is the exact solution.

The approximate solution is what we just wrote delta s c p, i ln T i by T 2 minus R l n p i by p 2, and all that we did here from the earlier relation was this part, where we said that c p the constant specific heat of ith component is constant, i not dependent on temperature. So, we have the relations that we have been looking for entropy change an approximate relation and a exact relation, so that completes all the properties that we have been looking for and the property changes that you are looking for a mixture.

So, at this point what we have achieved is what we did for a pure substance its counterpart for a mixture is what we have done. We have defined various properties, how did their change can be evaluated and seen one important thing that all properties can be expressed as a combination of mass or molar fractions, and the properties of the individual components at that condition. So, now you know the entire picture on as far as property it goes.

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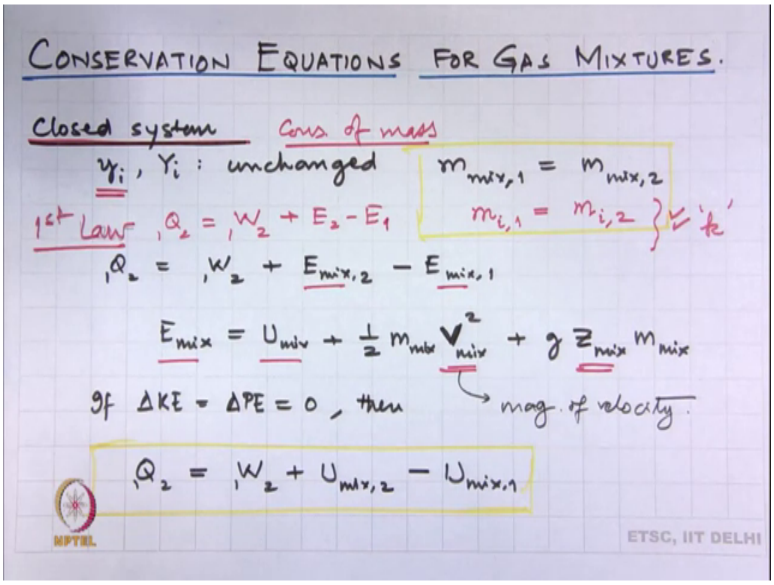

CONSERVATION EQUATIONS FOR GAS MIXTURES.

Closed system

Cons. of mass

y_i , Y_i : unchanged

$$\boxed{\begin{aligned} m_{mix,1} &= m_{mix,2} \\ m_{i,1} &= m_{i,2} \end{aligned}} \Big\} \checkmark\ 'k'$$

1st Law $_1Q_2 = {}_1W_2 + E_2 - E_1$

$$_1Q_2 = {}_1W_2 + E_{mix,2} - E_{mix,1}$$

$$E_{mix} = U_{mix} + \frac{1}{2} m_{mix} V_{mix}^2 + g Z_{mix} m_{mix}$$

mag. of velocity.

If $\Delta KE = \Delta PE = 0$, then

$$\boxed{_1Q_2 = {}_1W_2 + U_{mix,2} - U_{mix,1}}$$

Now, we will come to the last part of this module, which is similar to what we did for pure substance that how do I analyze a system where the working substance is a mixture, and not a pure substance. So, this is what we are looking at now is conservation equations for gas mixtures. The first thing, we will do is look at the closed system. So, what it means is that the system, there is no mass in flow or no mass out flow. And mass means in this case not just mixture mass, but no species is coming in or going out which means that during a process or given that system, the mixture masses remains constant.

And also mass of the ith component will be equal to mass of the ith component in state 2, so that is conservation of mass. The additional thing that has come here compared to pure substances is that instead of just one equation for conservation of mass which could be the mixture 1. We now we will have as many conservation equations as the number of components in the mixture.

Let us now look at the first law. What we had written for a pure substance was that Q 1 2 or in general what W 1 2 plus E 2 minus E 1, this is the most general form of this first law. And it did not differentiate whether the working substance was pure or a mixture.

Now, for a mixture we would modify these and say that Q 1 2 is W 1 2 plus E 2, we qualify it as being energy of the mixture in state 2 minus energy of the mixture in state 1, so that is the addition that is coming, where we define energy of the mixture as before internal energy of the mixture plus half kinetic energy of the mixture, which is mixture mass times its velocity of the square plus g z into m into mass, mass of the mixture multiplied by its elevation here. So, we are denoting a boldface V, this thick one to mean that this is magnitude of velocity, and not a vector.

And this is just to do differentiation that we already used the symbol V non-normal V, for volume. Now, in a closed system if there is no change in kinetic energy or potential energy, then the equation becomes simplified that Q 1 2 is W 1 2 plus U mix, 2 minus U mix, 1, so that becomes the operative form of the first law for a closed system, where the working substance is a mixture and this was the conservation of mass there.

So, in solving a problem this is exactly what we wanted, you how do I evaluate the internal energy of the mixture, and we just saw how this can be connected to the mass and molar fractions, and the component internal energies, so that is the a closed system. And the third thing that we have to do for the system is the second law analysis.

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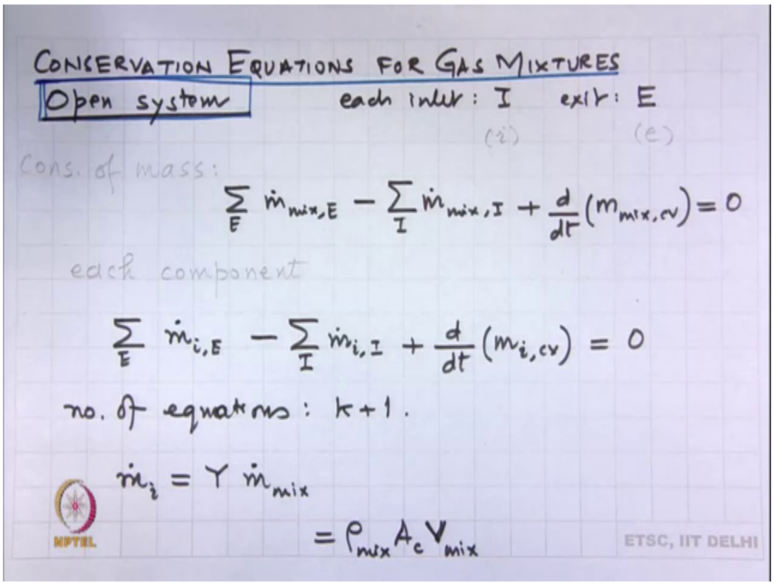

CONSERVATION EQUATIONS FOR GAS MIXTURES

Open system   each inlet : I (i)   exit : E (e)

Cons. of mass:

$$\sum_E \dot{m}_{mix,E} - \sum_I \dot{m}_{mix,I} + \frac{d}{dt}(m_{mix,cv}) = 0$$

each component

$$\sum_E \dot{m}_{i,E} - \sum_I \dot{m}_{i,I} + \frac{d}{dt}(m_{i,cv}) = 0$$

no. of equations : $k+1$.

$$\dot{m}_i = Y \dot{m}_{mix}$$
$$= \rho_{mix} A_c \mathbf{V}_{mix}$$

So, we are still looking at a closed system. And you say what is the second law analysis of a closed system, and this as we have known earlier S 2 minus S 1 is integral is greater than or equal to integral of delta Q by t equal to if the process is reversible, and greater than if it is irreversible. The modification that we need to make this relation for mixtures is that S 2 becomes S mix of 2 minus S mixture is state 1 greater than or equal to integral delta Q by T 1 to 2, so that is the second law for the closed system.

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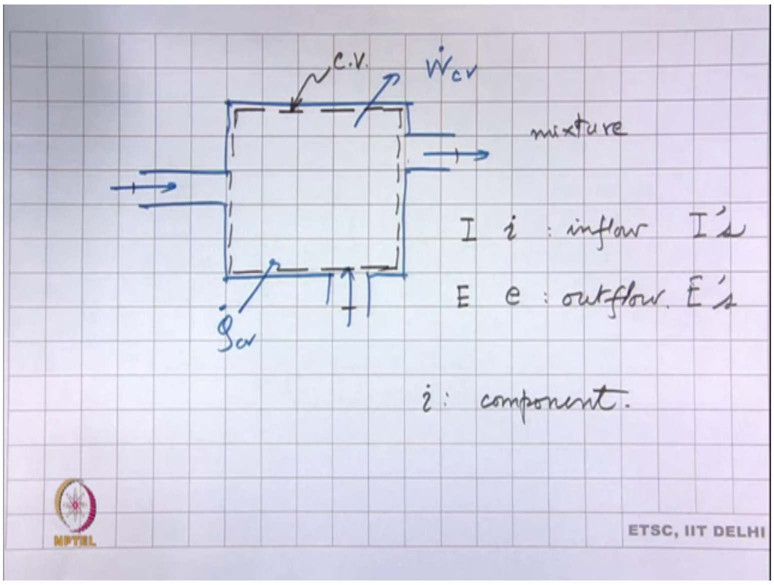

Now, we come to a conservation equations for gas mixtures for an open system. So, what we are doing here basically is like before we say that there is a system in to which there are different inflows and outflows across which, there could be heat transfer, and work transfer. And for that we define the control volume, which is say all this part of the substance in this control volume. The only difference is that these states here all of them would have a mixture.

If I need not be the case that every one of them would have a mixture, it could be that say for instance you have oxygen coming in from here, nitrogen coming from here, O 2 plus N 2 going out from here. So, we have two are pure substances one is a mixture or it could be that air comes in from here, you add something else flow it, and something else comes from here.

In doing the single fuel substance analysis, we identify these inflows by the subscript i, and by the subscript e for outflow. Now, we are running into a bit of a confusion, because i we have also just used to denote the component. So, the same subscript is coming is appearing for two things. And to avoid confusion, we are made a we will make a small change, and say that for inflows instead of i lower case, we will use uppercase I. And for outflows instead of using lowercase e, we will use capital E. So, thus control volume can have many inflows which are the i's and many outflows which are the E’s or any combination of them, in some of them can even be 0.

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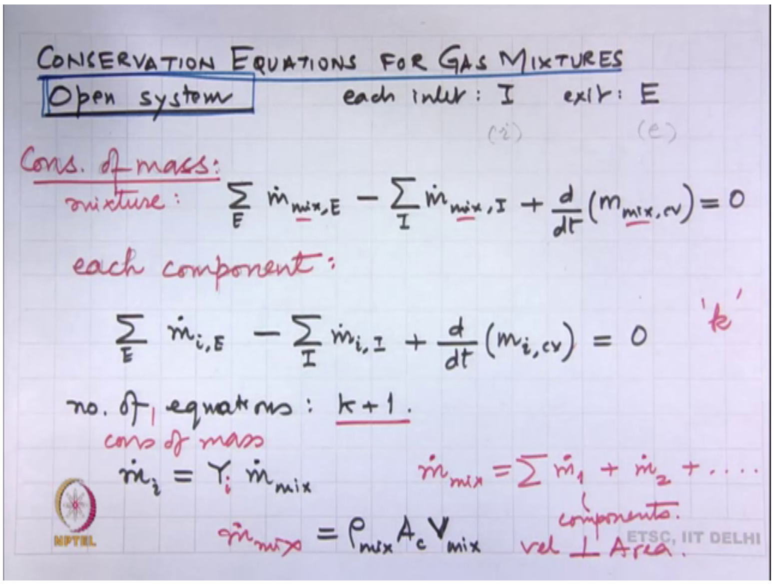

CONSERVATION EQUATIONS FOR GAS MIXTURES

Open system

each inlet : I (i) exit : E (e)

Cons. of mass:

mixture : $\sum_E \dot{m}_{mix,E} - \sum_I \dot{m}_{mix,I} + \frac{d}{dt}(m_{mix,cv}) = 0$

each component:

$$\sum_E \dot{m}_{i,E} - \sum_I \dot{m}_{i,I} + \frac{d}{dt}(m_{i,cv}) = 0 \qquad 'k'$$

no. of equations : k + 1.

cons of mass

$\dot{m}_i = Y_i \dot{m}_{mix}$

$\dot{m}_{mix} = \sum \dot{m}_1 + \dot{m}_2 + \ldots$ components.

$\dot{m}_{mix} = \rho_{mix} A_c V_{mix}$ vel ⊥ Area.

So, for this system with this notation, we can now write the conservation of mass and then we go on to the first law. So, conservation of mass for a mixture. So, their outflow rate minus inflow rate plus rate of accumulation of mass in the control volume equal to 0 that general form of the conservation of mass system good. Except that we are now adding a subscript there that out flow rates of the mixture minus inflow rates of each mixture plus rate of storage of mass in the mixture is equal to 0.

So, this is the mixture conservation of mass, but individually each component also has to conserve its mass. So, we can write conservation of mass equation for each component, and this time instead of mix, we only write for this specific component i. So, outflow rate of ith component minus inflow rate of ith component plus rate of storage of ith component in the control volume is equal to 0.

So, what it means is that we have a conservation equation one for the mixture, and one equation each for the k components that are there in the mixture. So, the total number of conservation of mass equations is k plus 1. And this is a major change from a pure substance being considered. And here now we are talking of rates mass inflow rate and outflow rate. And for each individual component, we can write that inflow rate is Y i times mixture mass flow rate. And that the mixture mass flow rate is summation of m dot 1 plus m dot 2 plus m dot 3. So, these are all the components.

So, at any flow when you have a mixture going in or flowing out, the total mixture mass flow rate is sum of the mass flow rates of the individual components that is what this is. And they can be related to by the mass the mass fraction. Also the mass flow rate of the mixture can be written like we did the mass flow rate of a pure substance, density into area into velocity of the mixture provided V is normal A c. So, the velocity is normal to the area, so that is conservation of mass for an open system.

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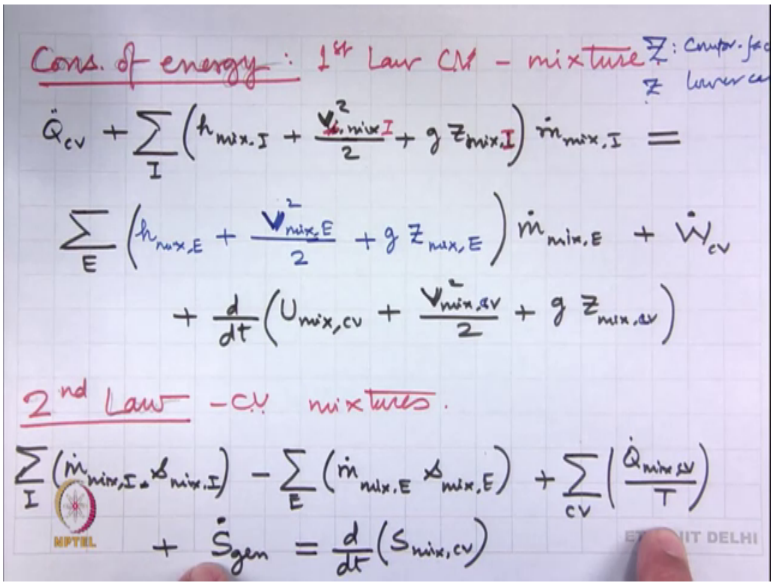

Cons. of energy : 1st Law CV – mixture

Z: Compr. fac

z lowerca

$$\dot{Q}_{cv} + \sum_{I}\left(h_{mix,I} + \frac{V^2_{mix,I}}{2} + g\,z_{mix,I}\right)\dot{m}_{mix,I} =$$

$$\sum_{E}\left(h_{mix,E} + \frac{V^2_{mix,E}}{2} + g\,z_{mix,E}\right)\dot{m}_{mix,E} + \dot{W}_{cv}$$

$$+ \frac{d}{dt}\left(U_{mix,cv} + \frac{V^2_{mix,cv}}{2} + g\,z_{mix,cv}\right)$$

2nd Law – CV mixtures.

$$\sum_{I}\left(\dot{m}_{mix,I}\, s_{mix,I}\right) - \sum_{E}\left(\dot{m}_{mix,E}\, s_{mix,E}\right) + \sum_{cv}\left(\frac{\dot{Q}_{mix,cv}}{T}\right)$$

$$+ \dot{S}_{gen} = \frac{d}{dt}\left(S_{mix,cv}\right)$$

Now, we write conservation of energy or the first law equation for a control volume. First law applied to a control volume, where inflow out flows are mixtures. So, the law that we had earlier is exactly the same, your Q dot c v as the first term. Then first this thing is the energy inflow rates, and right now we are writing it for the mixture. So, its m dot mixture for every inflow capital I, and the energy that it takes into the control volume, this is a specific enthalpy of the mixture for that state plus kinetic energy for that state, and potential energy for that state.

So, it is the mixture kinetic energy, this is the mixture potential energy plus there will be a similar term here for the exiting mass flow rates. And this we can write down as the mass flow rate here mixture exiting at each e h mix at E plus V square mixture at each exit divided by 2 plus g z mix at E. We do not have a confusion being the z’s here because for elevation z is lowercase, and capital Z was the compressibility factor. So, need to be clear that these are the lowercase sets ok. So, inflow rates is equal to outflow rate of energy plus work done by the control volume plus rate of storage of energy in the control volume which is U mix in the control volume plus V mix in the control volume plus elevation change of the control volume, so that is the conservation of energy for the control volume, it takes care of all those things.

And last thing left now is the second law for the same thing a control volume with mixtures. And again we do exactly the same thing that we did in the previous equation, we took the we take the equation for a pure substance or the most general form of the equation, and put the prefix mix wherever that is relevant. So, this is the entropy in flow rate for the mixture. So, there mass flow rate of mixture multiplied by its specific entropy out flow this is out in flow rates, out flow rates plus heat transfer through the control volume divided by the temperature plus rate of generation of entropy is equal to rate of storage of change of entropy in the control volume. This is exactly the same equation that we had for a single phase theory.

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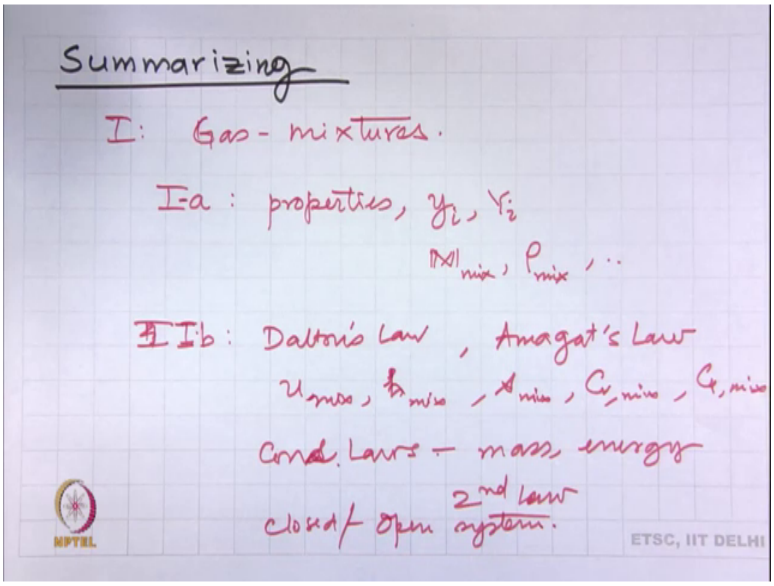

Summarizing

I: Gas - mixtures.

I-a : properties, y_i, Y_i

M_{mix}, ρ_{mix}, ..

I-b : Dalton's Law, Amagat's Law

u_{mix}, h_{mix}, s_{mix}, $C_{v,mix}$, $C_{p,mix}$

Cons. Laws - mass, energy

2nd Law

closed / open system.

So, we can now summarize, what we have got. In module 1, we did two parts now. Our objective of this module was to get gas mixtures was to study gas mixtures. And we started asking the question, how can I learn something from the pure substances and the formulations there, and extend that to gas mixtures. So, in first part of this module, we saw how we got some of the properties. We defined important property which was the mass and molar fractions, and using this we got the mixture molar mass the density of mixture.

And that set up the stage to go to the next level, where in the second module, we extended this knowledge using two laws Dalton's law of additive pressures, and Amagat's law of additive volumes. And using these and what we learned earlier, we were able to get the mixture properties u mix, h mix, s mix, C v mix, C p mix.

And then we went to the next stage, where we got the conservation laws conservation of mass, energy, and the second law. And we apply these and developed them for a closed system, and for an open system. So, we have now the complete process with us to take a problem apply this knowledge, and solve all the things that are required, when the working substance instead of being a pure substance is a mixture (Refer Time: 56:32).

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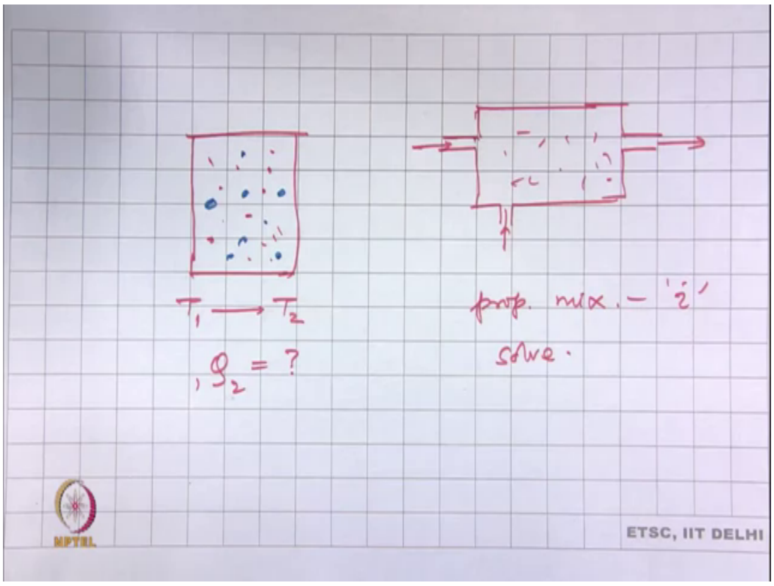

An example of such a thing would be that we have a system say a mixture of two things say one component is there, and second component is there. And if only one component was there we knew what would happen, if these were heated at constant volume from temperature T 1 to T 2, and the question we would ask is well what was Q 1 2. We will now if there is a mixture, we know what is the process to follow, how to get the properties of the mixture and answer the same question for this particular case.

Same thing we can do for an open system, where we can say that there is an inflow of something, and outflow something and how much is the accumulation happening there. For that also we know that we define the same way, we go to find the control volume all the approximations, see what is given get the properties of the mixture from the individual components, and then we can solve the problem. So, we have all the knowledge that we require now to solve problems involving gas mixtures particularly ideal gas mixtures, and in some cases even real gases, so that completes module 1 for gas mixtures, and we will stop here.

Thank you.