Fundamentals of Combustion

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Lecture – 05

Review of Basic Thermodynamics of Ideal Gas Mixtures Part – 02

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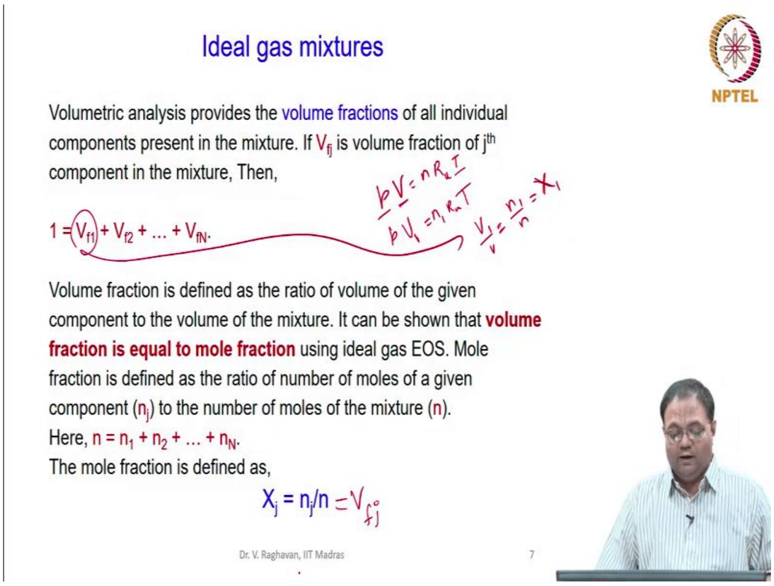

Ideal gas mixtures

Volumetric analysis provides the volume fractions of all individual components present in the mixture. If V_{fj} is volume fraction of j^{th} component in the mixture, Then,

$$1 = \boxed{V_{f1}} + V_{f2} + \ldots + V_{fN}.$$

$$\underline{p}\underline{V} = nR_uT$$

$$pV_1 = n_1R_uT$$

$$\frac{V_1}{V} = \frac{n_1}{n} = X_1$$

Volume fraction is defined as the ratio of volume of the given component to the volume of the mixture. It can be shown that **volume fraction is equal to mole fraction** using ideal gas EOS. Mole fraction is defined as the ratio of number of moles of a given component (n_j) to the number of moles of the mixture (n).

Here, $n = n_1 + n_2 + \ldots + n_N$.

The mole fraction is defined as,

$$X_j = n_j/n = V_{fj}$$

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So, you get the volume fractions ok. Now, volume fraction is equal to mole fraction. Actually we can easily prove that by using Amagat's law of partial volumes. When we use that we can prove that the volume fraction is nothing but the mole fraction.

For example, see we can write like this. So, when you conduct an experiment in which see for example, you have $pV = nR_uT$.

Now I make a constant pressure device. Assume that we have a frictionless piston acting on a cylinder and try to inject the mixture into this so that it occupies a volume V and let the pressure be constant at p and temperature is T for the mixture. When you maintain the pressure as p and temperature as T, you will know what is the volume occupied by the mixture.

R_u also is known to you. Now, this will be the equation which will be obeyed by the mixture, when it occupies the volume V exerting a pressure p at a temperature T. Now, I remove this mixture and by the volumetric analysis I know what are the volume fractions of individual gases. It will say that CO is this much, CO_2 is this much, O_2 is this much and so on.

So, volume fractions of each and every component present in the mixture will be identified and we will know that. So, you know the components now, try to inject one of the component here. Now, while doing so, keep the same pressure. So, p is maintained same. Similarly, I will keep the temperature same, R_u is also same.

Now, this component 1 will occupy different volume for the same pressure and temperature. Volume occupied by the component 1 is say V_1. So that means, I can calculate n1, which is the number of moles of component 1. So, if you divide this you will get V_1/V equal to n_1/ n.

So; that means, V_1/V is what? Volume fraction of the first component, correct. So, V_1/V, I know this. Now, this is nothing but the mole fraction. I will say mole fraction of the first component X_1 that is it.

So, volume fraction is defined as the ratio of the volume of the given component to the volume of the mixture. So, now I have shown that volume fraction is equal to mole fraction. So, the volumetric analysis gives the volume fraction which is nothing but the mole fractions and if you add all the mole fractions you will get 1, ok.

So, mole fraction, what is mole fraction? It is defined as the ratio of the number of moles of the given component. So, for example, here the number of moles occupied by the first component is n_1 divided by the number of moles occupied by the mixture is n.

So, n_1/n is X_1. Similarly, for any component, say j^{th} component, X_j is n_j/n that is it. So, mole fractions are defined.

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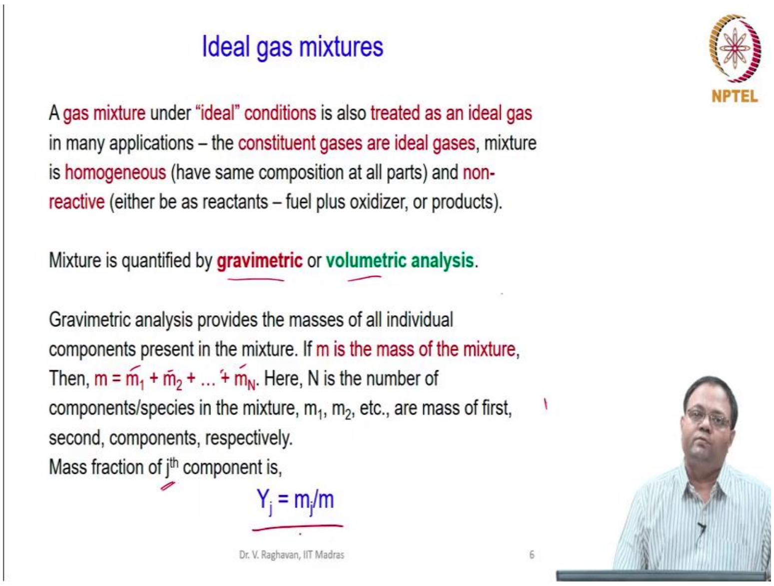

Ideal gas mixtures

A gas mixture under "ideal" conditions is also treated as an ideal gas in many applications – the constituent gases are ideal gases, mixture is homogeneous (have same composition at all parts) and non-reactive (either be as reactants – fuel plus oxidizer, or products).

Mixture is quantified by **gravimetric** or **volumetric analysis**.

Gravimetric analysis provides the masses of all individual components present in the mixture. If m is the mass of the mixture, Then, $m = m_1 + m_2 + \ldots + m_N$. Here, N is the number of components/species in the mixture, m_1, m_2, etc., are mass of first, second, components, respectively.
Mass fraction of j^{th} component is,

$$Y_j = m_j/m$$

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So, previous slide we have defined mass fraction, which is nothing but m_1/m is the mass fraction of the first component and so on. Similarly, here by volumetric analysis I have got volume fractions and we have proved that the volume fraction is nothing but the mole fraction. So, use that and get the mole fractions directly. This is nothing but what? This can be written as V_{fj}, volume fraction of the j^{th} component that is it ok. So, we have now quantified the mixture either in terms of mass or in terms of moles; volume fraction which is nothing but mole fraction.

So, we know the once you subject the mixture to volumetric or gravimetric analysis you get mole fractions and mass fractions ok that is what we have got now.

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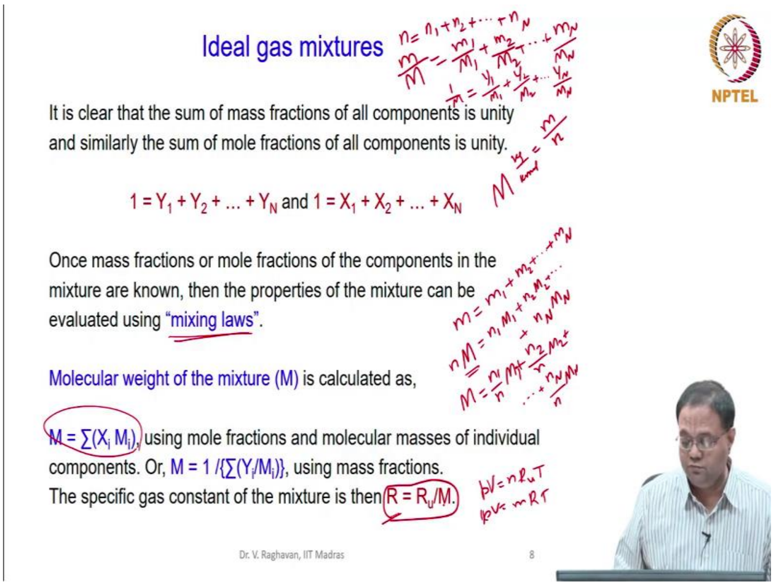

Ideal gas mixtures

It is clear that the sum of mass fractions of all components is unity and similarly the sum of mole fractions of all components is unity.

$$1 = Y_1 + Y_2 + \dots + Y_N \text{ and } 1 = X_1 + X_2 + \dots + X_N$$

Once mass fractions or mole fractions of the components in the mixture are known, then the properties of the mixture can be evaluated using "mixing laws".

Molecular weight of the mixture (M) is calculated as,

$M = \sum(X_i M_i)$, using mole fractions and molecular masses of individual components. Or, $M = 1/\{\sum(Y_i/M_i)\}$, using mass fractions.

The specific gas constant of the mixture is then $R = R_u/M$.

$n = n_1 + n_2 + \dots + n_N$

$\frac{m}{M} = \frac{m_1}{M_1} + \frac{m_2}{M_2} + \dots + \frac{m_N}{M_N}$

$\frac{1}{M} = \frac{Y_1}{M_1} + \frac{Y_2}{M_2} + \dots \frac{Y_N}{M_N}$

$M \frac{kg}{kmol} = \frac{m}{n}$

$m = m_1 + m_2 + \dots + m_N$

$nM = n_1 M_1 + n_2 M_2 + \dots + n_N M_N$

$M = \frac{n_1}{n} M_1 + \frac{n_2}{n} M_2 + \dots + \frac{n_N M_N}{n}$

$pV = n R_u T$

$pV = m R T$

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Anyway, this identity you know that when you add all the mass fractions you will get 1, unity. Similarly, when you add all the mole fractions you will get 1, unity. So, like volumetric fractions, if we add you get 1. Now, how will you calculate properties related to mixture once the components of the mixture are known?

For that we use what is called mixing laws. So, once mass fractions or mole fractions of the components of the mixture are known then the properties of the mixture can be evaluated using mixing laws. So, first what I will try to do is try to calculate the molecular weight of the mixture. Molecular weight of the mixture can be calculated with these expressions.

So, we can easily do this. For example, you know for the mixture you can write like this. So, m, mass of the mixture will be equal to m_1 + m_2 + …. and so on to m_N, which is nothing but the individual masses are summed up will give you the mixture mass. Now, see molecular weight M is in kilo gram per kilo mole.

This means I can write this as the mass of the component divided by mass of the mixture divided by the number of moles or the mixture, kg per kilo mole correct. So, now, I will substitute mass. I write mass in terms of moles. So, I will write this as n × M, M is capital M is the molecular mass, small m is the mass of the mixture.

Similarly, write for this n_1M_1 + n_2M_2 + … and so on to + n_NM_N. Now, I want the molecular weight of the mixture, this is unknown. Now, divide this equation by n.

So, we will get molecular weight of the mixture is nothing but $(n_1/n) \times M_1$ + $(n_2/n) \times M_2$ + … and so on to $(n_N/n) \times M_n$.

So, that is what I have written here; $\sum(n_i/n)M_i$ is the mole fraction of individual components into their molecular weight. So, $\sum X_iM_i$, X_i is nothing but the mole fraction of the component into its molecular weight and I am summing up all these.

So, when I sum up the products of mole fraction of the component with its molecular weight and sum it up then you get the mixture molecular weight. So, that is what the proof for this equation is.

Once I know this is a mixing rule, this is the basic mixing rule by which weighted average of the molecular weights are taken based upon the mole fractions. Why I am taking here X_i because this is per mole, kg per kilo mole. So, I am just equating this and writing like this.

Now, you can ask when volumetric fractions are known, mole fractions are known, so, I can do this. If I do the gravimetric analysis, I only know the mass fractions. So, how will I calculate molecular weight? Again, start with this. For example, I can do this, now I can write this $n = n_1 + n_2 + \ldots$ and so on like this correct.

Now, we can write what I want to replace n by m. Now, what is done? n equal to number of moles equal to mass by molecular mass. So, this I can write as this divided by mass by molecular mass.

Similarly, for individual components $m_1/M_1 + m_2/M_2 + \ldots.$ and so on to m_N/M_N. Now, divide by mass. So, $1/M = Y_1/M_1 + Y_2/M_2 + \ldots.$ and so on.

So, that is 1/M will be equal to Y_1/M_1 that is what I have written here. So, $M = 1/\sum Y_i/M_i$, Y_i by M_i. So, that is what I have written here. So, first thing is you have to calculate the molecular weight of the mixture.

Once you know the mole fractions or mass fractions use one of these equations and calculate that. Once you do that the specific gas constant of the mixture is nothing but universal gas constant divided by the molecular mass of the mixture; so, $R = R_u/M$, ok. That is what we were seeing. So, the first step you have to do is to calculate this.

Once you know this then I can very easily write the equation of state as $pV = nR_uT$ or $pV = mRT$. Now, you know R. So, we can now use this relationship. Whatever way you want you can use this relationship and you have now got the value of R and molecular weight of the mixture.

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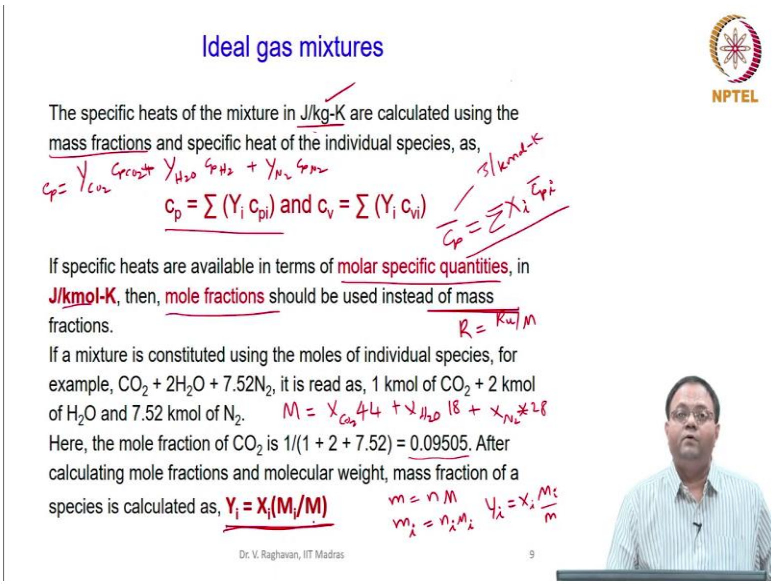

Ideal gas mixtures

The specific heats of the mixture in J/kg-K are calculated using the mass fractions and specific heat of the individual species, as,

$c_p = Y_{CO_2} c_{pCO_2} + Y_{H_2O} c_{pH_2} + Y_{N_2} c_{pN_2}$

$c_p = \sum (Y_i c_{pi})$ and $c_v = \sum (Y_i c_{vi})$

J/kmol-K

$\overline{c_p} = \sum X_i \overline{c_{pi}}$

If specific heats are available in terms of molar specific quantities, in **J/kmol-K**, then, mole fractions should be used instead of mass fractions.

$R = R_u / M$

If a mixture is constituted using the moles of individual species, for example, $CO_2 + 2H_2O + 7.52N_2$, it is read as, 1 kmol of CO_2 + 2 kmol of H_2O and 7.52 kmol of N_2.

$M = X_{CO_2} 44 + X_{H_2O} 18 + X_{N_2} * 28$

Here, the mole fraction of CO_2 is 1/(1 + 2 + 7.52) = 0.09505. After calculating mole fractions and molecular weight, mass fraction of a species is calculated as, $Y_i = X_i(M_i/M)$

$m = nM$

$m_i = n_i M_i$

$Y_i = X_i \frac{M_i}{M}$

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Now, calorific equation of state that is you want to find these specific heats. Please understand that again the same weighted average can be used. Now, you have to select appropriate equations here. See for example, when you want to calculate the specific heat of the mixture in mass basis Joule per kg Kelvin, then you have to use mass fractions.

So, for example, you know individual C_p values of every component in the mixture ok. C_{pi} is the specific heat of the ith component at constant pressure that into its mass fraction; $Y_i \times C_{pi}$ then sum it up for all the species you will get the C_p of the mixture. Similarly, C_v, you can do this or if you find the C_p of mixture then R is known. So, $C_p - C_v = R$, you can use that to find C_v.

This is done using mass fractions because I want a quantity which is mass specific, that is per kg. On other hand if we have specific heats in molar basis. For example, $\overline{C_{pi}}$ I want to calculate of the mixture then I will use $X_i \overline{C_{pi}}$.

This $\overline{C_{pi}}$ is the molar specific heat at constant pressure of the ith species that multiplied by the mole fraction and summed it up for the all the species, you will get the C_p of the mixture in molar basis. So, this unit is here per kilo mole correct, instead of kg or you can also do this $C_p \times M$ you will give this.

So, C_p and C_v are related by molecular weight also. But if you have mole fractions and if you have the molar specific heats known then you can straight away use this rule to find this. Mole fraction should be used when you have a molar specific quantities.

So, now we want only such properties. Now, we will try to take a small example and try to see how we are going to go about the calculations of mass fractions and so on ok. One more thing is mass fraction and mole fraction are related like this. This is very simple to prove $Y_i = X_i \times M_i / M$.

So, we can very easily do this proof. For example, I say this m, in kg, equal to number of moles, kilo moles, into kg per kilo mole molecular weight. This is for the mixture. If I write for any component say ith component m_i, we can write as $n_i \times M_i$, capital M is the molecular mass.

So, now you divide this we will get $Y_i = n_i/n$ is $X_i \times M_i/M$. So, that is the way you get this relationship between the mass fraction and the mole fraction. Now, let us consider here a mixture of products which is coming out of combustion of some fuel.

So, basically this is typically when you combust methane with adequate air ok, only what is required for full combustion you get these products. CO_2 1 mole 2 moles of H_2O and 7.52 moles of N_2. So, I will define why I get this later, but this is the products I have. It is at some temperature T and some pressure p.

Now, when I write the mixture like this, I can read it as 1 mole or 1 kilo mole; say like kg when I say mass, I only use SI units kg. If I want specifically say its gram or milli gram etcetera we have to specifically say that. So, normally mass is represented in kg in SI units. Similarly, the number of moles is represented by kilo moles; so, kmol.

So, 1 kilo mole of CO_2 plus 2 kilo mole of H_2O plus 7.52 kilo mole of N_2. So, that is the number of moles of each component that should be, so, this equation is read like that. So, here the mole fraction of CO_2 is calculated by it has 1 mole and total number of moles is 1 + 2 + 7.52.

So, 1 / (1+ 2 + 7.52), the mole fraction of CO_2 will be 0.09505. For example, nitrogen will have the highest mole fraction because it its number of moles is 7.52 out of 1 + 2 + 7.52. Now, for this mixture let us calculate enthalpy of the mixture.

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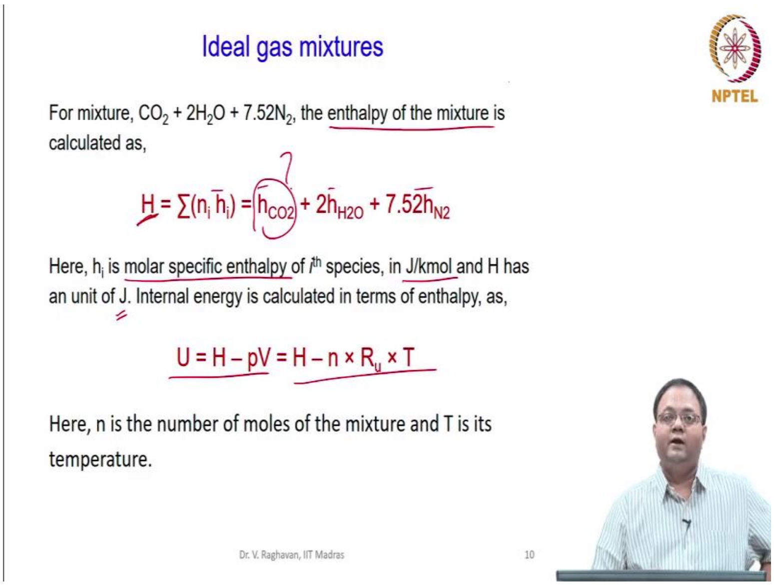

Ideal gas mixtures

For mixture, $CO_2 + 2H_2O + 7.52N_2$, the enthalpy of the mixture is calculated as,

$$H = \sum (n_i \bar{h}_i) = \bar{h}_{CO2} + 2\bar{h}_{H2O} + 7.52\bar{h}_{N2}$$

Here, h_i is molar specific enthalpy of i^{th} species, in J/kmol and H has an unit of J. Internal energy is calculated in terms of enthalpy, as,

$$U = H - pV = H - n \times R_u \times T$$

Here, n is the number of moles of the mixture and T is its temperature.

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So, now you can also substitute everywhere. See for this mixture, you can calculate mole fraction of each component like this. Similarly, once the mole fraction is known how we calculate molecular weight? You calculate mole fraction of CO_2, mole fraction of H_2O, mole fraction of N_2 then use this equation. Go back and use this equation when mole fractions are known.

So, molecular weight of this mixture will be here. Molecular weight of this mixture will be equal to mole fraction of CO_2 times molecular weight of CO_2 that is 44 plus mole fraction of H_2O times molecular weight of H_2O is 18 plus mole fraction of N_2 times molecular weight is 28.

So, this is where you calculate the molecular weight of the mixture. Then you can find from mole fractions the mass fractions. Whenever you want that you can find that. Then molecular weight of the mixture is known. So, you can find R of the mixture as R_u/M. So, for this mixture let us calculate. So, now, C_p how you will calculate for this mixture, you have to know individual C_p values.

So, for example, C_p of CO_2 you should know, C_p of H_2O you should know and C_p of N_2 you should know, either on mass basis or molar basis. Once you know that then you substitute this in this equation. So, now, you have calculated mole fractions, molecular weight of the mixture. So, mass fractions can be calculated.

If you have C_p's in terms of mass basis then you can use this equation here and substitute the C_p's of individual components. So, for this you can write for example, here for this mixture you can write C_p as like this.

So, if you have molar basis C_p then you have to replace the mass fraction by the mole fraction and put an overhead bar to indicate that that is molar based quantity.

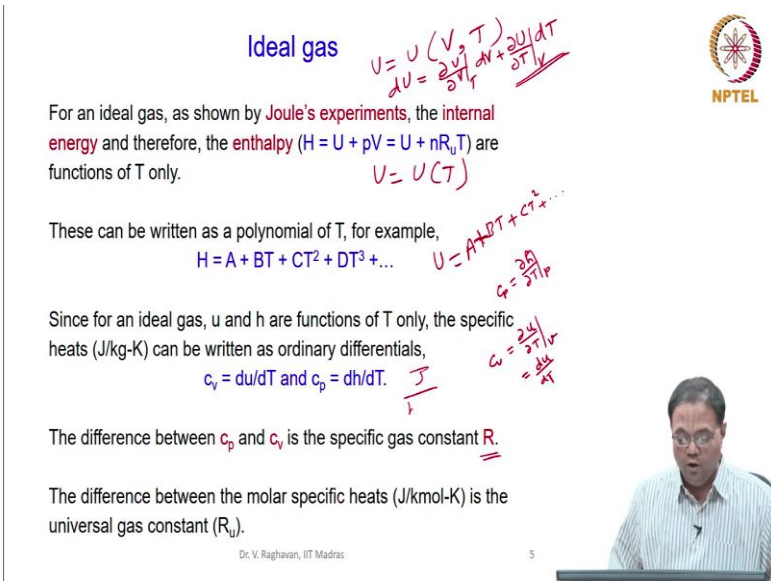
This is the way you calculate all these properties. Now, how will you calculate the enthalpy of the mixture? Enthalpy of the mixture is calculated by using what is called molar specific enthalpy. So, actually I can also put an overhead bar.

So, since I have specified clearly, I did not use that. So, H is the enthalpy of the mixture, it is nothing but $\sum n_i h_i$ ok. Now, this is you have 1 mole of CO_2. So, $1\times h_{CO_2}$ + $2\times h_{H_2O}$ + $7.52\times h_{N_2}$ that's it. These are molar based quantities.

So, how will you calculate this? This we will cover later ok. How will you calculate the enthalpy of individual species, I will let you know later. So, because this has some definition, standard enthalpy definitions, I will come to that when you do the heat calculations.

Now, molar specific, see that is what I have written here h_i is the molar specific enthalpy of ith species in Joule per kilo mole. So, when you multiply by the number of species number of moles of each component you will get the H in Joules.

Once you know H, see normally we calculate H then you recalculate the value of U using the definition of H. H = U + pV. So, you calculate U as H - pV. So, that is what we try to do here. Now, for calculating pV use the equation of state. This is the way you calculate all the property. This is about the ideal gas and the ideal gas mixtures. (Refer Slide Time: 19:39)



Ideal gas

$U = U(V, T)$

$dU = \frac{\partial U}{\partial V}\Big|_T dV + \frac{\partial U}{\partial T}\Big|_V dT$

For an ideal gas, as shown by Joule's experiments, the internal energy and therefore, the enthalpy ($H = U + pV = U + nR_uT$) are functions of T only.

$U = U(T)$

These can be written as a polynomial of T, for example,

$$H = A + BT + CT^2 + DT^3 + \ldots$$

$U = A + BT + CT^2 + \ldots$

$c_p = \frac{\partial h}{\partial T}\Big|_p$

Since for an ideal gas, u and h are functions of T only, the specific heats (J/kg-K) can be written as ordinary differentials,

$$c_v = du/dT \text{ and } c_p = dh/dT.$$

$\frac{J}{k}$

$c_v = \frac{\partial u}{\partial T}\Big|_v = \frac{du}{dT}$

The difference between c_p and c_v is the specific gas constant R.

The difference between the molar specific heats (J/kmol-K) is the universal gas constant (R_u).

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So, ideal gas I will just quickly summarize.

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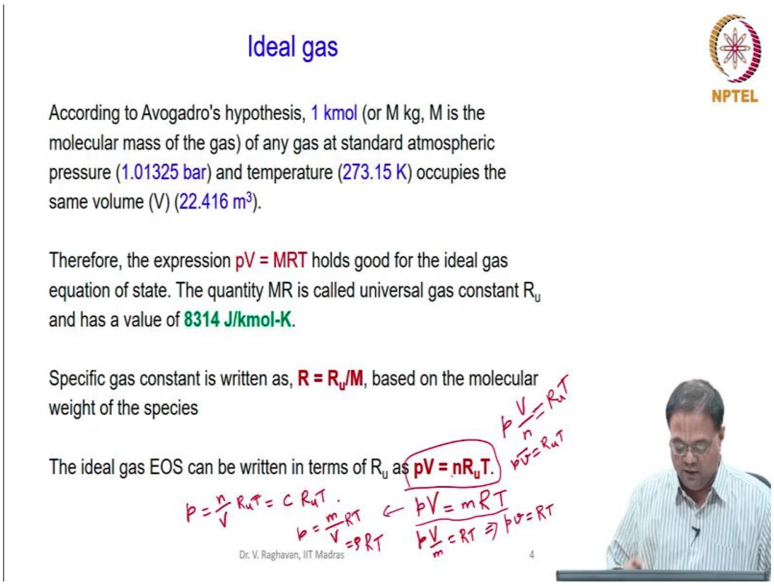

Ideal gas

According to Avogadro's hypothesis, 1 kmol (or M kg, M is the molecular mass of the gas) of any gas at standard atmospheric pressure (1.01325 bar) and temperature (273.15 K) occupies the same volume (V) (22.416 m^3).

Therefore, the expression pV = MRT holds good for the ideal gas equation of state. The quantity MR is called universal gas constant R_u and has a value of **8314 J/kmol-K**.

Specific gas constant is written as, **$R = R_u/M$**, based on the molecular weight of the species

The ideal gas EOS can be written in terms of R_u as $\boxed{pV = nR_uT.}$

$p\frac{V}{n} = R_uT$

$p\bar{v} = R_uT$

$p = \frac{n}{V}R_uT = C R_uT.$

$p = \frac{m}{V}RT = \rho RT \leftarrow pV = mRT$

$p\frac{V}{m} = RT \Rightarrow pv = RT$

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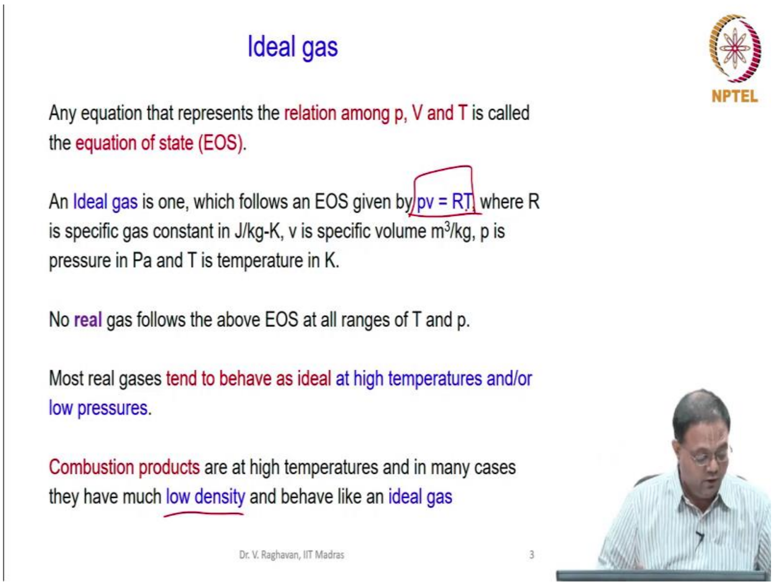

Ideal gas

Any equation that represents the relation among p, V and T is called the equation of state (EOS).

An Ideal gas is one, which follows an EOS given by $\boxed{pv = RT}$ where R is specific gas constant in J/kg-K, v is specific volume m^3/kg, p is pressure in Pa and T is temperature in K.

No real gas follows the above EOS at all ranges of T and p.

Most real gases tend to behave as ideal at high temperatures and/or low pressures.

Combustion products are at high temperatures and in many cases they have much low density and behave like an ideal gas

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Ideal gas is a real gas which obeys a simple equation of state like this, under specific conditions where its density is low, so that the intermolecular forces between the molecules are negligible and volume occupied by the molecules are also negligible under this condition.

Then you can see that the gases obey this equation of state; p, V is specific volume based on mass, pV = RT, R is the specific gas constant. So, this is the equation and this equation can be written in several forms like pV = nR_uT or pV = mRT, R is a specific gas constant and so on.

Even $p = \rho RT$, $p = CR_uT$, several ways you can write this equation and this is a simple equation which is obeyed and relates p V and T. This is possible only when ideal gas assumption is valid under certain ranges of temperature and pressure, where the densities are low enough.

Now, another thing is in calorific equations of state, one more simplification is possible that the internal energy and enthalpy are functions of temperature only. That means, you can write H as a polynomial of temperature or U as a polynomial of temperature and so on.

And the advantage is the C_p and C_v are written as ordinary derivatives of the enthalpy and the internal energy, respectively. $C_p - C_v = R$. So, these are the fundamental equations which are obeyed by an ideal gas. And if I have a mixture, ideal gas mixture each and every constituent of the mixture is an ideal gas.

If so, the mixture also behaves like an ideal gas that means, obeying that same PVT relationship, what we have shown before. What are the constituents in the mixture is quantified by gravimetric or volumetric analysis. When you say gravimetric analysis, I can get the individual masses of each species; m_1, m_2 to m_N.

And masses are directly got and you know the total mass which is examined. So, you will get the mass fractions of all the species. Mass fraction of a component is equal to mass of the component divided by the mass of the mixture. Then by volumetric analysis you will get the volume fractions of each and every component.

And we have just shown here that the volume fraction is nothing but the mole fraction by a simple experiment. When you want to keep the pressure and temperature constant and see what is volume occupied by a particular gas mixture or individual gases then you can show that the volume fraction is equal to the mole fraction.

And in that case, you can see that you can write the mole fraction as volume fraction; n_j/n that is the mole fraction of the j^{th} component is nothing but number of moles occupied by the j^{th} component divided by total number of moles which is nothing but the volume fraction which you measured in volumetric analysis.

Now, the identity is important. Identities are $\sum Y_i = 1$, $\sum X_i = 1$. Now, once you know the components of the mixture, how will you get the properties of the mixture? other properties which are required for us are got using mixing laws.

First and foremost property what you will try to evaluate is the molecular weight of the mixture which is nothing but $M = \sum X_i M_i$ that is mole fraction of individual component multiplied by its own molecular weight summed up for all the species which will give you the molecular weight of the mixture.

Similarly, you can use the mass fractions. Mass fraction divided by its molecular weight and summed up its reciprocal will be equal to the molecular mass of the mixture. So, once you know the molecular weight I can calculate a specific gas constant of the mixture, R_u/M ok.

So, I have just tried to derive these equations here and coming to the specific heats, specific heat of the mixture. So, first of all you have to know what the individual specific heat is.

So, by measurement lot of correlations are available, tables are available and we can take individual C_p values from those and once you know that if it is mass based, so, Joule per kg kelvin, then you have to use mass fractions and get the C_p of the mixture as $\sum Y_i C_{pi}$ and here C_p is in Joule per kg Kelvin, but on other hand if you have molar basis.

For example, Joule per kilo mole Kelvin then mole fractions have to be used instead of mass fractions and you get this. $\overline{C_p} = \sum X_i \overline{C_{pi}}$, where this overhead bar represent that it is molar based quantity.

Now, if you get a mixture like this, say mixture has some moles. Any equation is actually written in terms of number of moles only as a standard practice.

So, when you have a mixture like say 1 kilo mole of CO_2 plus 2 kilo moles of H_2O and 7.52 kilo moles of N_2 then you can calculate the total number of moles by summing up the number of moles in each component and mole fraction can be found by dividing the number of moles of individual component to the number of total number of moles.

Like for example, for CO_2, it is 1 by 1 + 2 + 7.52 ok and so on. Once the mass fraction is known, mole fraction can be calculated or otherwise if mole fraction is known mass fraction can be calculated by using this equation; $Y_i = X_i \times M_i/M$, where this M_i is the individual molar mass divided by the molar mass of the mixture.

So, the enthalpy of the mixture is calculated by just summing up. Enthalpy of the mixture is actually calculated using what is called molar specific enthalpies which is in Joule per kilo mole and multiply that molar specific enthalpy of an individual species with its own number of moles ok. So, $n_i h_i$ and sum it up of for all the species, you will get the that the enthalpy of the mixture H in Joules. Now, internal energy can be calculated using the definition of the enthalpy, $H - pV = U$. So, that will be and pV can be replaced by the equation of state. So, this is the way you calculate the properties of ideal gas mixtures.