

Fundamentals of Combustion
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Lecture – 04
Review of Basic Thermodynamic of Ideal Gas Mixtures Part – 01

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- (2) Review of basic thermodynamics of ideal gas mixtures
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Let us move on to the second topic, Review of Basic Thermodynamics of Ideal Gas Mixtures.

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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 $pv = RT$, where R is specific gas constant in $J/kg\cdot K$, 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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A definition of ideal gas basically comes like this. The fundamental properties pressure, volume and temperature are related by what is called equation of state. So, any equation which relates these three properties, we call it equation of state. And ideal gas equation of state is very simple in nature.

For example, I can write ideal gas equation of state as $pV = RT$. So, here pressure into volume will be equal to RT , where this volume is specific in nature; the specific volume, v , is the total volume capital V divided by the mass. The unit of specific volume is meter cube per kg.

When you say a gas behaves like an ideal gas; then this obeys this particular equation for its p , V , T relationship, where this R is called a specific gas constant. We can write this equation in several other ways. The main content here is, when the gas behaves like an ideal gas, then this simple p , V , T relationship holds good.

But in general, no gas is going to be a perfect ideal gas. So, no real gas will follow the above equation of state in all range of temperature and pressure, only under certain conditions it will behave like an ideal gas. Now, when you have very high temperatures, low to moderate pressures; then we will get densities to be at a low to moderate value.

Now, coming to our combustion products; combustion products are at very high temperatures; and even if pressures are somewhat low to moderate, the densities are not going to be high. When the gas density is very low, then the molecules are not very close to each other.

So, they hit with each other and move apart and they are always not very close to each other. When they are very close to each other the molecules ripple each other.

As the separation distance increases, the repulsive forces decrease and it becomes an attractive force and that becomes a maximum at a particular separation distance. As the separation distance increases, see I am saying average separation distance, if that is increased, then what happens is the attraction forces or the repulsive forces becomes negligible. We can say intermolecular forces between these two molecules tends to 0.

Under those conditions, a gas behaves like an ideal gas, obeying this equation of state. So, all the gases are real in nature and they will not obey this under every circumstances. Only when the densities are very low, temperatures are very high or pressures are low to moderate, this law is obeyed. At low to moderate pressures and high temperatures; you can see that the densities are low enough, so that the intermolecular forces are negligible. In such cases, a gas behaves like an ideal gas. If this gas is not a single gas, but a mixture of gases then the mixture itself will behave like an ideal gas. So, combustion products are

mixture of several gases; but due to the high temperature prevailing there the mixture density will be low enough. So, the combustion products can be qualified as an ideal gas mixture.

In an ideal gas mixture, all the gases are ideal gases and they obey this equation of state given by $pV = MRT$, or $pV = RT$. So, this is the introduction to ideal gas.

In our course, we are going to deal with combustion products or even in reactants for example; they are not going to be at extremely high pressures. So, the densities are lower enough and we can assume that the reactants or products will behave like an ideal gas.

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Ideal gas

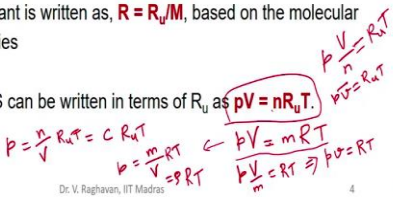
According to Avogadro's hypothesis, 1 kmol (or M kg, M is the molecular mass of the gas) of any gas at standard atmospheric pressure (1.01325 bar) and temperature (273.15 K) occupies the same volume (V) (22.416 m³).


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 $pV = nR_uT$.







According to Avogadro's, hypothesis, 1 kilo mole, or M kg of the gas at standard atmospheric pressure (1.01325 bar) and temperature of 273.15 Kelvin, 0 degrees, occupies same volume. This is given by 22.416 m³. Now, $pV = MRT$, holds good for ideal gas.

This is the equation state, I am just trying to write in this way; the quantity MR is called the universal gas constant R_u . It has a value of 8314 J/kmol-K. Specific gas constant can be written as $R = R_u/M$. The molecular weight has a unit of kg/kmol.

If you divide the universal gas constant the by molecular weight, you will get a specific gas constant which has a unit of J/kg-K. So, you can write the ideal gas equation of state in terms of universal gas constant given by $pV = nR_uT$. This temperature should be in Kelvin.

This n is the number of moles occupied by a particular gas or gas mixture; total number of moles occupied by the gas mixture. p is the pressure exerted by the mixture and volume occupied by the mixture is V. The temperature of the mixture is capital T.

If you want to change it to mass basis; then you can write this as $pV = mRT$. So, this is another way to write the equation of state. Now dividing this volume by mass, we can write, $pV/m = RT$, which implies $pv = RT$.

This is the equation of state, which is very simple in nature and ideal gas alone obeys this under certain circumstances in the range of temperature and pressures, where the densities are low enough. So, there are several ways right the equation of state. We can also this as $pV/n = R_u T$.

Now, this V/n is in $m^3/kmol$. This is the molar specific volume. This can be written as $\bar{V} = R_u T$. This is molar specific volume $m^3/kmol$. You can also do this, $p = (n/V)R_u T$.

Now, this n/V in $kmol/m^3$, is the concentration. So, this can be written as $cR_u T$. This c , is the concentration, that is number of moles which is occupying a given volume V .

Similarly, I can write this as $p = (m/V)RT$. The unit of this m/V is kg/m^3 , that is density. So, there are several ways of writing the equation of states.

Here you can see, $p = \rho RT$ or $p = cR_u T$. So, whenever you write the equation in molar basis; you will see that the universal gas constant appears. Whenever you write in mass basis, then the specific gas constant will appear. So, the ideal gas, or each ideal gas in a mixture or the mixture itself will behave like an ideal gas and obey these equations of states written in any form.

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Ideal gas

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


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


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,

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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$$U = U(V, T)$$

$$dU = \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial V} dV$$

$$U = U(T)$$

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

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

$$c_v = \frac{\partial u}{\partial T}$$

$$c_p = \frac{\partial h}{\partial T}$$

$$c_p - c_v = R$$

Now, what about other properties? We have connected three important properties namely; pressure, volume and temperature. A simplistic equation like this $pV = MRT$ or $pV = nR_u T$ can be used to relate pressure, volume. So, any two properties if we know,

the third property can be found out. This is the way you relate the three fundamental properties, pressure, volume and temperature.

Now, other properties, like internal energy, enthalpy for ideal gas, we have lot of simplifications. Normally if you take, internal energy is not only a function of temperature; it is also a function of a volume. So, internal energy can be written in terms of V and T. For example, I can write here $U = U(V,T)$.

Any two properties can be used to write this. This means that, when you want to find the change in U; you have to write this as, $dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$.

If you write like this, you will see that for every real gas, this is obeyed. However, by Joule's experiment, Joule has constructed experiments and he has considered several materials and several conditions and he found that the internal energy for an ideal gas is dependent only on temperature. That means for ideal gas U is a function of T only, not V.

This is one of the important aspects of ideal gas, one more simplified equation you get. You do not need to have a partial derivative. Now, you can very easily write this as, U is a function of T only. So, any change in U will be dU/dT .

Similarly, enthalpy is a derived property, $U + pV$. You will note that U and this pV can be now expressed in terms of equation of state. Say for example, I will take the molar based relation $pV = nR_u T$. So, $H = U + nR_u T$. Since U is a function of temperature alone, H also will be a function of temperature only.

For all other gases we can write $H = H(p,T)$. But now you can see that by Joules experiment for ideal gases, the dependence of enthalpy on pressure is not there. So, enthalpy will be dependent only on temperature.

Similarly, internal energy is only function of temperature, so you can evaluate that. If you write H or even U as a polynomial of T, for example, $U = A + BT + C T^2 \dots$

Now, just add the fourth term $nR_u T$. This can be absorbed with another coefficient B. So, H also can be written in terms of this polynomial.

Now, specific heat at constant volume or specific heat at constant pressure, can be found by these equations. For example, the specific heat at constant volume, c_v , is defined as $(du/dT)_v$. This is a specific property.

So, dou capital U by dou T at v constant volume; when you use this U is divided by mass, you will get a specific heat. So, specific heat at constant volume is defined as

partial derivative of u with respect to temperature when v is constant. However, for ideal gas, this partial derivative disappears and you write du by dT .

Similarly, h , small h is the specific enthalpy. So, capital H divided by mass. So, the specific heat at constant pressure c_p is the derivative of h with respect to temperature that is it; it is an ordinary derivative, we do not need to use the partials as per the definition

$c_p = \left(\frac{dh}{dT} \right)_p$. But since for an ideal gas h is dependent only on temperature; this partial derivative can be written as the ordinary derivative like this.

So, these are specific properties and very important for us; for our problems we have to calculate c_v , c_p etcetera as a function of temperature. So, once you know enthalpy or internal energy written in terms of temperature, we can use that and calculate the c_p and c_v values.

Now, if we do this, $c_p - c_v = R$. Now, please understand, there are this; when I say c_p and c_v , they are mass based quantities, that means the units of this is Joule per kg Kelvin. I have written here.

So, its units is Joules per kg Kelvin; we can also write in terms of moles, like Joule per kilo mole Kelvin, just divide this by the molecular mass. Then whenever we use molar quantities, we use a overhead bar. So, when I say \bar{c}_v overhead bar; that means its unit is Joule per kilo mole Kelvin. So that is the way you write. So, now, when you subtract c_p and c_v ; so, c_p minus c_v will be equal to the specific gas constant; because it is written in mass basis.

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Ideal gas


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

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

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,


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).



Handwritten notes:

$U = U(V, T)$
 $dU = \frac{\partial U}{\partial V} dV + \frac{\partial U}{\partial T} dT$
 $U = U(T)$
 $H = A + BT + CT^2 + DT^3 + \dots$
 $U = A + BT + CT^2 + \dots$
 $c_p = \frac{dH}{dT}$
 $c_v = \frac{dU}{dT}$
 $c_p - c_v = R$



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If you do c_p bar minus c_v bar, you get R_u . So, this is molar basis. So, this is the way you write. So, that is what the difference between molar specific heat will give you the universal gas constant. So, the equation of state is simple enough.

So, $pV = nR_uT$ and even you can see that dependence of internal energy, enthalpy etcetera is only with temperature, not with any other properties like volume or pressure. The c_v and c_p are not as partial derivatives of u and h respectively anymore and they are ordinary derivatives.

So, these are all the advantages of this assumption, ideal gas assumption. And it is not only an assumption; it actually good enough for our combustion calculation, because of the low densities involving high temperatures.

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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, $m = m_1 + m_2 + \dots + m_N$. Here, N is the number of components/species in the mixture, m_1, m_2, \dots , are mass of first, second, components, respectively.

Mass fraction of j^{th} component is,

$$Y_j = m_j/m$$

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So, now, a gas mixture we will consider now; ideal gas conditions, that means all the constituents of this gas mixture, each and every constituent is an ideal gas. So, if I have a mixture of says O_2 and N_2 that is a standard air; it can be taken as ideal gas for practical purposes, because it the temperature is say 25 degree centigrade and pressure is only at 1 atmosphere.

Very low pressure, densities are not very high; so, its density is say 1.2 kg per meter cube approximately. So, now at this low density, air will behave as an ideal gas; this is because the oxygen and nitrogen both behave as an ideal gas.

So, the air itself will behave as an ideal gas. When each and every constituent of the mixture is an ideal gas; then the mixture itself will behave as an ideal gas. Now, how will you analyse the mixture?

The first one is we have to first quantify the mixture. See as I told you now, air contains some amount of oxygen, some amount of nitrogen; first of all we should know what is the amount. So, that is done by two type of analysis; one is called gravimetric analysis, and other is called volumetric analysis.

Gravimetric analysers are actually costlier devices; but they give mass of each component present in the mixture. For example, if there are N , capital N components; then by doing a gravimetric analysis, you will get masses of individual components. For example, if m is the total mass of the mixture; then I will get $m = m_1 + m_2 + m_3 \dots + m_N$. if you add up you will get m .

So, you take a mixture of mass m and subject it to gravimetric analysis; it will give individual components present in that.


And the mass of individual components are m_1 to m_N and if you add it will you will get the mixture mass. So, this is obeyed. And you can see that, when you divide this total equation by m , you get an identity.

Now, from this equation I can define, what is called a mass fraction? For example, take j^{th} species, it can be any species. So, take j^{th} species; the mass fraction of the j^{th} component is mass of that species divided by the mass of the mixture.

So, $Y_j = m_j/m$, small m . So, this is called mass fraction Y_i . I am using here; Y_i or Y_j here will be equal to m_j by m , mass fraction of an individual component. So, that is.

So, we normally deal with the mass fractions, mole fractions, volume fractions etcetera. (Refer Slide Time: 21:57)

Ideal gas mixtures



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


$$1 = V_{j1} + V_{j2} + \dots + V_{jN}$$

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

The mole fraction is defined as,

$$X_j = n_j/n$$



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Now similar to the gravimetric analysis, we can also conduct volumetric analysis which are cheaper actually; volumetric analyser is a cheaper analyser, but it will give volume fractions of the constituents present in this.

So, it will take some amount of volume of gas and it will give the volume fractions of the individual gases present in this. This is actually accomplished by having some columns in which a particular gas will be absorbed.

So, here when the mixture passes through these columns; a particular gas is absorbed in each column, so that we will know what is the volume of the gas which is absorbed. So, eventually you get the volume fraction of the mixture. So, if V_{fj} , V suffix f_j is the volume fraction of the j^{th} component; then we can add all of this.

For example, $V_{f1} + V_{f2} + \dots + V_{fN} = 1$, capital N is the number of the components present in the mixture.

Now, volume fraction I can get by experiments. So, you use the mixture in a gravimetric analyser or a volumetric analyser and you can get either the mass fractions directly or volume fractions.

Now, we can write the equation of state, for example, as $pV = MRT$ here. This can be applied to a mixture. So, what is a pressure p here?

Pressure p exerted by the mixture; capital V is volume occupied by the mixture, m is the mass of the mixture and this R is the specific gas constant for the mixture, and the mixture occupies the temperature of T . So, I can apply this and find some relationship out of this.

Now, if you have volume fractions; where you will apply that volume fractions? Because you have another equation which is nothing, but $pV = nR_u T$

So, for the mixture, pressure is known total volume occupied by the mixture is known; n is the number of moles occupied by the mixture, universal gas constant and temperatures are known. So, how will you measure number of moles? So, you cannot do this.

So, if you get volume fractions what you will do with that? Mass fraction if you get, at least know what I will do is; I can write this equation and I can take a volume in which, for example, I can take only one component and see if the the mass of the component is measured to be m_1 . So, I will try to see how much volume it occupies, how much pressure it exerts and so on for a given temperature.

So, I will get some equation for that. So, basically the mass fraction is directly got. So, that is easy for us and all other properties, I will try to correlate in terms of mass fraction itself. So, that is the important advantage of getting the gravimetric analysis.

But when you do a volumetric analysis; how will you translate the volume fractions into mole fractions? See for example, small n is the number of moles of the mixture; but each and every component can only have some number of moles.

And if you add all the masses, you get the total mass of the mixture; when you add each and every number of moles of the individual components, you will get the total number of moles.

So, can you translate the volume fraction into mole fraction? So, that is what the question is.