Fundamentals of Combustion for Propulsion
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Lecture - 04
Equilibrium

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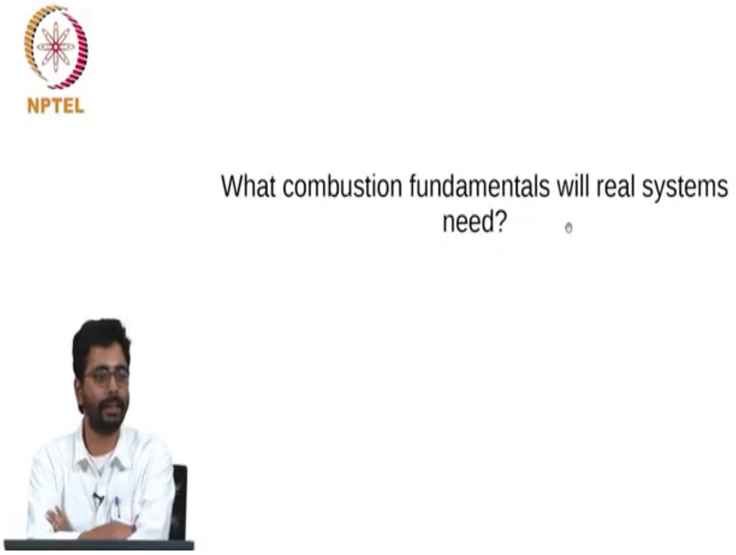

What combustion fundamentals will real systems need?

Let us continue. The first session, we got an overview of variety of combustion systems which are relevant to propulsion and a couple of examples which are not directly relevant to propulsion also. But the idea was to give you an overview of what fundamental aspects of combustion are required to deal with real systems.

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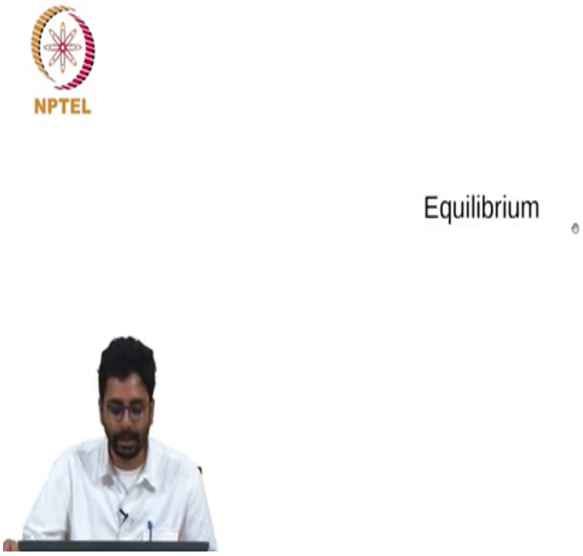

Equilibrium

What we will do in this lecture is we will look at one such fundamental aspect which will be the idea of equilibrium. Generally, we will be talking about thermodynamic equilibrium and we will also see a couple of examples of how calculating equilibrium states is of relevance to actual systems.

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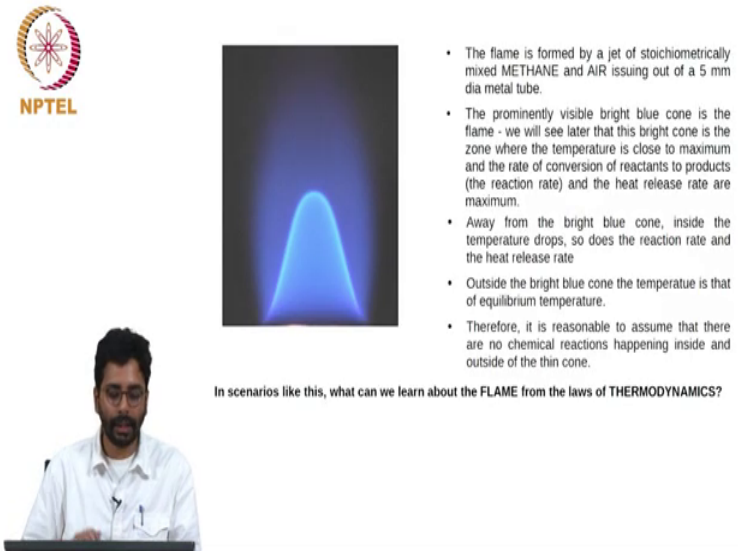

- The flame is formed by a jet of stoichiometrically mixed METHANE and AIR issuing out of a 5 mm dia metal tube.
- The prominently visible bright blue cone is the flame - we will see later that this bright cone is the zone where the temperature is close to maximum and the rate of conversion of reactants to products (the reaction rate) and the heat release rate are maximum.
- Away from the bright blue cone, inside the temperature drops, so does the reaction rate and the heat release rate
- Outside the bright blue cone the temperatue is that of equilibrium temperature.
- Therefore, it is reasonable to assume that there are no chemical reactions happening inside and outside of the thin cone.

In scenarios like this, what can we learn about the FLAME from the laws of THERMODYNAMICS?

I will use this, I will use the picture of a premix methane air flame that you see in the screen as sort of a working example for introducing ideas related to equilibrium. So, this flame that you see in the picture is formed by a jet of close to stoichiometrically mixed methane and air. It is a pre mixed flame and the mixture is issuing out of a 5 millimeter diameter metal tube from the bottom. The fuel air mixture is coming from here and ignited at the top and a flame a conical flame forms at the top of the burner.

What I referred to as flame just now is what you see in the picture of the flame, which is the prominently visible bright blue cone that is the flame. We will see later that this bright cone is the zone, where the temperature is close to maximum and the rate of conversion of reactant to product, we will refer to as reaction rate and the heat release rate because of conversion of the reactants to products are maximum.

So this is this zone the blue cone; bright blue cone that you see here. Away from the bright blue cone on either side which is inside of the cone and the outside on either side of the bright blue cone, the temperature is lower than what it is at the flame and so, are the reaction rates and heat release rate ok. And therefore, it is reasonable to assume that there are let be not say no chemical reactions, but there are reaction rates away from the flame are orders of magnitude smaller than the reaction rates at the flame.

So, there are essentially no chemical reactions happening inside and outside of the thin cone. We of course, the accurate way of saying it is in outside of the cone what do you have is a condition of equilibrium, where the forward and react backward reaction rates are exactly matched. But we come to that later. So, the question that we are interested in is in scenarios like this. What is it that we can learn about the flame from the laws of thermodynamics? So, that is the first fundamental idea that we will discuss in this lecture.

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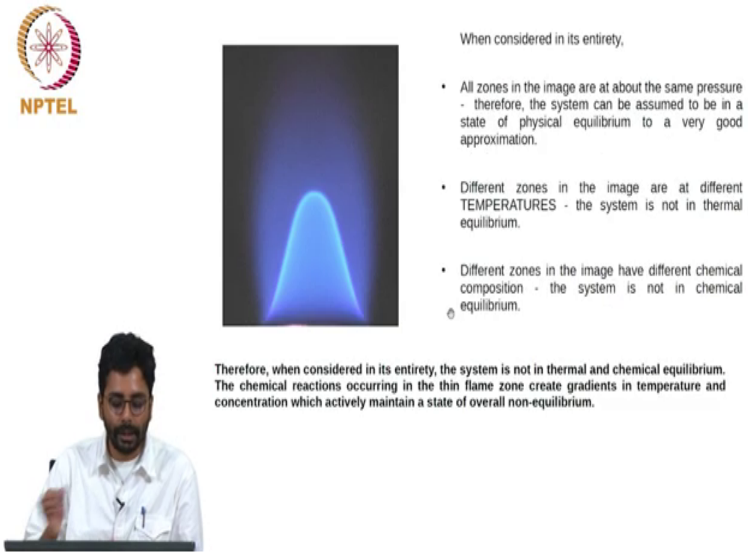

When considered in its entirety,

- All zones in the image are at about the same pressure - therefore, the system can be assumed to be in a state of physical equilibrium to a very good approximation.
- Different zones in the image are at different TEMPERATURES - the system is not in thermal equilibrium.
- Different zones in the image have different chemical composition - the system is not in chemical equilibrium.

Therefore, when considered in its entirety, the system is not in thermal and chemical equilibrium. The chemical reactions occurring in the thin flame zone create gradients in temperature and concentration which actively maintain a state of overall non-equilibrium.

So, can considered in its entirety as a full system, all zones in the image that you see are at about the same pressure. It is jet of methane and premix mixture of methane and air issuing into open atmosphere. And therefore, the pressure everywhere is roughly the same, except for small differences in pressure that are required to establish the flow which is a few Pascal's at maximum and compared to the atmospheric pressure of hundred-thousand Pascal's, that variation is very small.

So, if you calculate the pressure as density times the gas constant times temperature. It will be the same everywhere. Therefore, the system can be assumed to be in a state of physical equilibrium to a very good approximation. What we mean by that is the pressure everywhere is roughly the same. But different zones in the image are at different temperatures obviously the system is not in thermal equilibrium. For example, the temperature as we saw in the previous slide close to the flame is much higher than it is elsewhere ok.

Also different zones in the image have different chemical composition ok. Inside the cone you have predominantly reactance, at the flame the reactants are getting converted into products, outside of the flame you have products of combustion ok. So, the system is not in chemical equilibrium, the system is not in thermal equilibrium, but system to a very good approximation is it physical equilibrium ok.

So, when considered as a single entity, the system is not in thermal and chemical equilibrium. In fact, the chemical reactions occurring in the thin flame zone creates gradients in temperature and concentration which actively maintain a state of overall non equilibrium.

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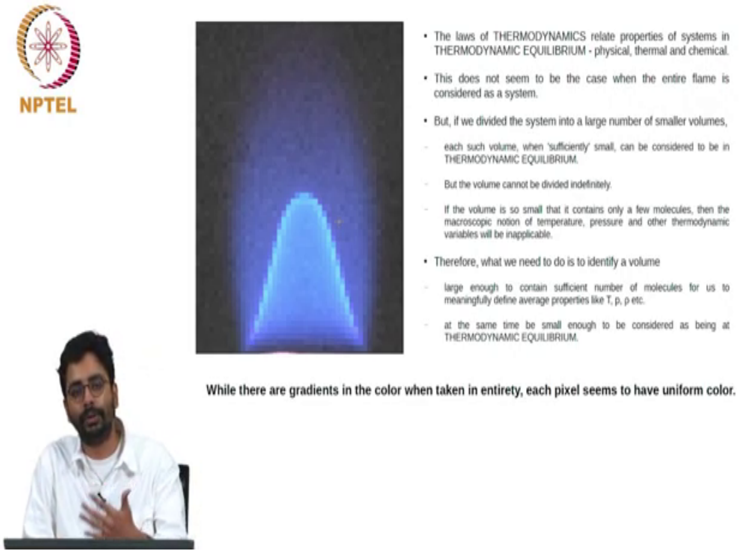

- The laws of THERMODYNAMICS relate properties of systems in THERMODYNAMIC EQUILIBRIUM - physical, thermal and chemical.
- This does not seem to be the case when the entire flame is considered as a system.
- But, if we divided the system into a large number of smaller volumes,
  - each such volume, when 'sufficiently' small, can be considered to be in THERMODYNAMIC EQUILIBRIUM.
  - But the volume cannot be divided indefinitely.
  - If the volume is so small that it contains only a few molecules, then the macroscopic notion of temperature, pressure and other thermodynamic variables will be inapplicable.
- Therefore, what we need to do is to identify a volume
  - large enough to contain sufficient number of molecules for us to meaningfully define average properties like T, p, ρ etc.
  - at the same time be small enough to be considered as being at THERMODYNAMIC EQUILIBRIUM.

While there are gradients in the color when taken in entirety, each pixel seems to have uniform color.

But we all know from our courses in thermodynamics that thermodynamics or the laws of thermodynamics relate properties of systems in thermodynamic equilibrium ok. At the system has to be in a state of physical, thermal and chemical equilibrium for us to use the laws of thermodynamics to relate different properties of the system. But this does not seem to be the case when the entire flame is considered as a system because it is not in thermal and chemical equilibrium.

But what we could do is if we divided the system into a large number of smaller boxes ok, such that each small box or each small volume can be considered to be in thermodynamic equilibrium. This box has to be sufficiently small, we will precisely define what should what we mean by sufficiently small for it to be considered in terms of thermodynamic equilibrium.

Of course, the volumes cannot be divided indefinitely because we know that if the volume is so small that it contains only a few molecules, then the macroscopic notions of temperature density and other thermodynamic variables will become inapplicable ok. Therefore, what we need to identify, what we need to do is to identify a volume which is large enough to contain sufficient number of molecules for us to meaningfully define average properties of temperature, pressure and density. But it should be at the same time be small enough to be considered at same temperature, same pressure and same chemical composition. So, the laws of thermodynamics can be used.

So, this idea is what does conveyed by this pixelated image of the same flame, where each pixel can be considered to be at thermodynamic equilibrium, while the entire system is not in thermodynamic equilibrium. So, an indicator of this is the gradients and color when taken as a whole system, but each pixel been considered as a unit seems to have uniform color. The same can be taken as representation of uniform temperature and composition.

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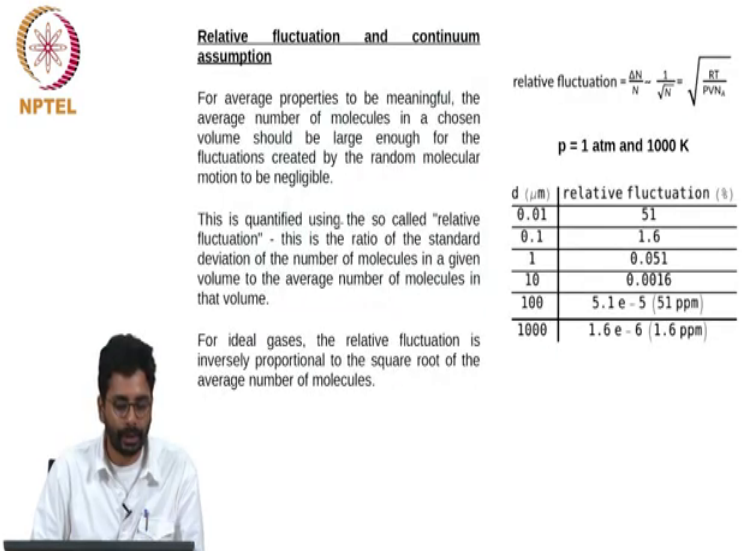

Relative fluctuation and continuum assumption

For average properties to be meaningful, the average number of molecules in a chosen volume should be large enough for the fluctuations created by the random molecular motion to be negligible.

This is quantified using the so called "relative fluctuation" - this is the ratio of the standard deviation of the number of molecules in a given volume to the average number of molecules in that volume.

For ideal gases, the relative fluctuation is inversely proportional to the square root of the average number of molecules.

$$\text{relative fluctuation} = \frac{\Delta N}{N} \sim \frac{1}{\sqrt{N}} = \sqrt{\frac{RT}{PVN_A}}$$

p = 1 atm and 1000 K

d (μm)	relative fluctuation (%)
0.01	51
0.1	1.6
1	0.051
10	0.0016
100	5.1 e - 5 (51 ppm)
1000	1.6 e - 6 (1.6 ppm)

So, that. So, we will address the two aspects separately; one is how small the volume can be and how large. So, what is the lower limit and what is the upper limit. Lower limit so that thermodynamic averages can be meaningfully defined. Upper limit so that the thermodynamic equilibrium assumption is valid. So, we will look at the lower limit first.

So, for average properties to be meaningful, the average number of molecules in a chosen volume should be large enough for the fluctuations created by random molecular motion to be negligible ok. This idea is quantified using what is called relative fluctuation, which is nothing but the ratio of if you take a small volume. The Relative fluctuation is nothing but the ratio of the standard deviation of the number of molecules or fluctuation or measure of fluctuations in the molecular concentration to the average number of molecules in that volume ok.

So, relative fluctuation is defined as the measure of the fluctuation and the number of molecules in a chosen volume divided by the total number of, the average number of molecules in that volume. For ideal gases this quantity varies as 1 by square root of N; N is the number of molecules which are present in the small volume which we know from ideal gas equation of state goes like this square root of RT over PV times N A; N A is the Avogadro constant. This about 6 into 10 rises to 23.

So, when we calculate or we can estimate the relative fluctuation using this relationship for a typical case which is pressure of one atmosphere and the temperature of 1000 Kelvin's. As you can see if you choose a volume which has let us say imagine a cube with the side of 0.01 micron, the relative fluctuation is very large about 51 percent large number of molecules go out and come in.

So, the molecular number of molecules and the volume fluctuate a lot, when you have a volume that is as small as 0.01 micron and the as the number of as the size of the cube increases and we get to about the micron, the fluctuation has come down by a large factor. It is now only 0.051 percent.

And when you get to a one mm cube, the relative fluctuation is for every million molecules only about 2 molecules leave on an average to volume. So,. So, starting from about 0.1 micron, we can consider the volume to have sufficiently large number of molecules with minimal fluctuation for averages to be meaningfully defined ok. So, so with this we can now, we now have a limit on what the smallest volume can be.

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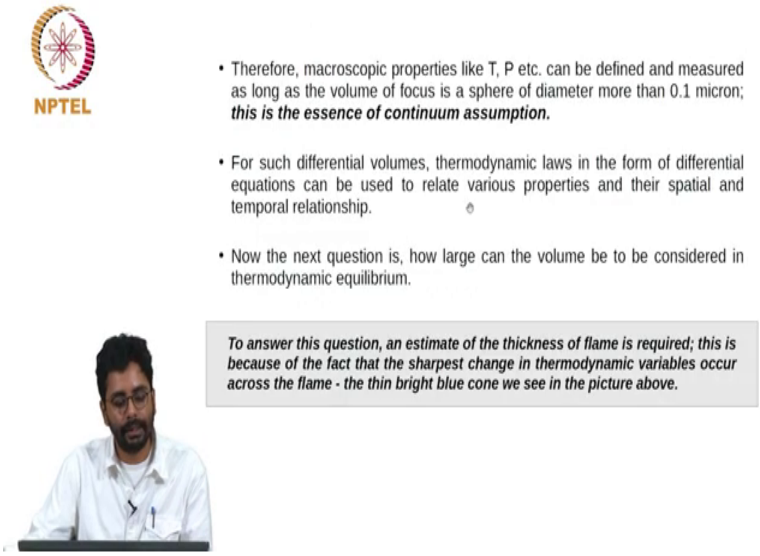

- Therefore, macroscopic properties like T, P etc. can be defined and measured as long as the volume of focus is a sphere of diameter more than 0.1 micron; ***this is the essence of continuum assumption.***
- For such differential volumes, thermodynamic laws in the form of differential equations can be used to relate various properties and their spatial and temporal relationship.
- Now the next question is, how large can the volume be to be considered in thermodynamic equilibrium.

To answer this question, an estimate of the thickness of flame is required; this is because of the fact that the sharpest change in thermodynamic variables occur across the flame - the thin bright blue cone we see in the picture above.

Therefore, macroscopic properties like temperature and pressure can be defined and measured as long as the volume of focus is a sphere or a cube whichever is convenient for you to imagine, you can take that. I think cubes are easier because that is how we divide the domains when we do computational simulations ok. So, a cube of side not more than sorry of size more than 0.1 microns. When we have more than 0.1 microns, at 0.1 microns relative fluctuation is about 21.6 percents and then, it drops very quickly as the volume increases.

So, as long as the size is more than about 0.1 micron, we do not have to worry about the validity of the average properties. This in essence is the continuum assumption and for such differential volumes, Thermodynamics Laws in the form of differential equations can be used to relate various properties and the spatial and temporal relationships which we call as the

Navier-Stokes Equation which we use for stimulating flows and reactions through different commercial systems.

Now, we can move on to the next limit which is how large can the volume be to be considered in thermodynamic equilibrium. But to answer this question, we need to have some estimate of length scale of relevance to flames which we will call the thickness of the flame. This is because of the fact that sharpest change in thermodynamic variables occur across the flame, a thin bright blue cone we see in the picture which we saw in the picture in the previous slide. The thickness of that entity is the thickness over which the variables change significantly and therefore, we need to make sure that the volumes that we choose are smaller so that the changes are not large ok. So, a good measure of that size is the thickness of the flame. So, what does the thickness of the flame?

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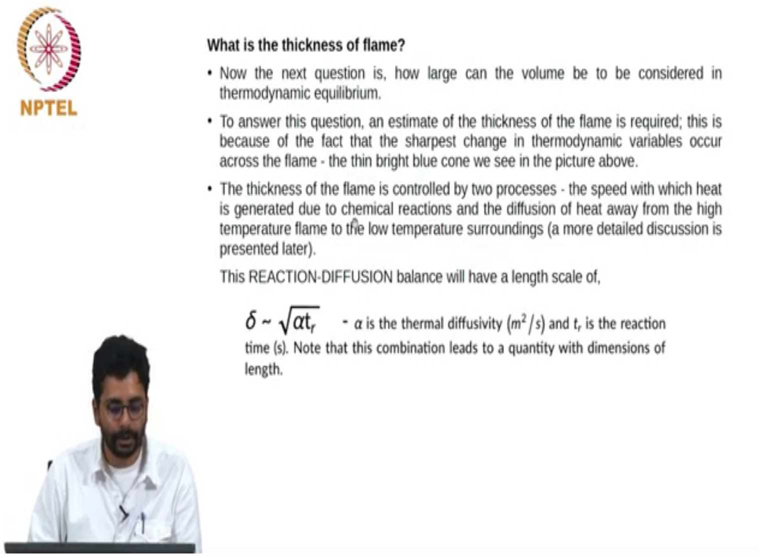

What is the thickness of flame?

- Now the next question is, how large can the volume be to be considered in thermodynamic equilibrium.
- To answer this question, an estimate of the thickness of the flame is required; this is because of the fact that the sharpest change in thermodynamic variables occur across the flame - the thin bright blue cone we see in the picture above.
- The thickness of the flame is controlled by two processes - the speed with which heat is generated due to chemical reactions and the diffusion of heat away from the high temperature flame to the low temperature surroundings (a more detailed discussion is presented later).

This REACTION-DIFFUSION balance will have a length scale of,

$\delta \sim \sqrt{\alpha t_r}$ - α is the thermal diffusivity (m^2/s) and t_r is the reaction time (s). Note that this combination leads to a quantity with dimensions of length.

That is an question. To answer this question, we need an estimate of the flame thickness. This is because of the fact that well I am repeating this point the sharpest changes in thermodynamic variables occur across the flame ok, the thin bright blue cone we saw in the pictures above ok. This is something important this is something that we will use many times in this course.

The thickness of the premix flame that we are looking at is controlled by two processes; one is the speed with which heat is generated due to chemical reactions ok, which raises the temperature in the domain and the other processes is the diffusion of heat away from the high temperature flame to the low temperature surroundings. What I mean by that is remember that when you set up the experiment in a lab, you have a steady blue flame and if you measure the temperature of the flame, it does not change with time.

But the products the reactants are continuously getting converted into products and heat is being generated and unless the heat is removed from the reaction zone at about this at the same rate, the temperature cannot remain steady ok. That this that the temperature remains steady means that heat is removed at the same rate that it is being generated and this process this balance is what does maintaining the temperature profile ok.

So, this reaction diffusion balance, we will have a length scale which like for any reaction diffusion process we will go as square root of diffusivity multiplied by a timescale ok. The alpha is the thermal diffusivity measured in meter squared per second and tr; t subscript r is reaction time. This is also another feature that you will see in analysis of mass transport, heat transport and momentum transport. Whenever the process is controlled by a diffusion reaction balance, the length scale associated with the process will be proportional to square root of diffusivity times at timescale.

Here, the relevant diffusivity is the diffusion coefficient of heat and the relevant times I am sorry that the diffusivity that is relevant as the thermal diffusivity. The relevant timescale is the reaction time scale.

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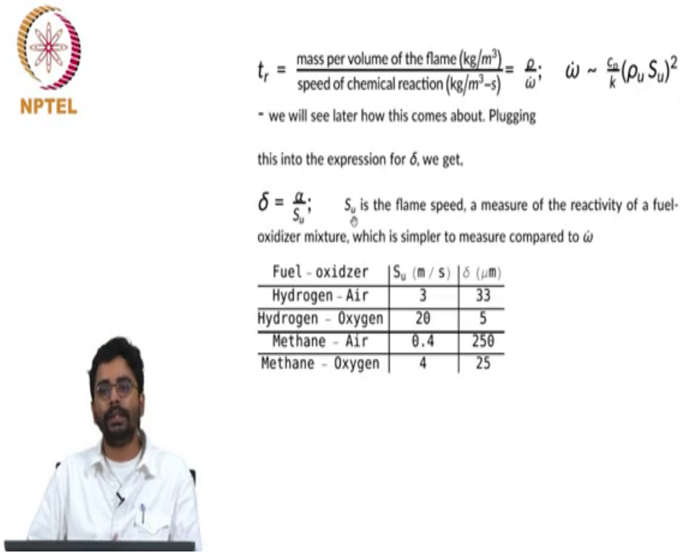

$$t_r = \frac{\text{mass per volume of the flame } (kg/m^3)}{\text{speed of chemical reaction } (kg/m^3\text{–}s)} = \frac{\rho}{\dot{\omega}}; \quad \dot{\omega} \sim \frac{c_p}{k}(\rho_u S_u)^2$$

- we will see later how this comes about. Plugging

this into the expression for δ, we get,

$\delta = \frac{\alpha}{S_u}$; S_u is the flame speed, a measure of the reactivity of a fuel-oxidizer mixture, which is simpler to measure compared to $\dot{\omega}$

Fuel - oxidzer	S_u (m / s)	δ (μm)
Hydrogen - Air	3	33
Hydrogen - Oxygen	20	5
Methane - Air	0.4	250
Methane - Oxygen	4	25

A time scale associated with reaction is simply the you have a small volume where reactants are getting converted into products. So, the time for reaction is simply the amount of reactance percent and that volume divided by the rate at which the reactions are getting consumed ok. So, the timescale for the reaction is the mass inside a chosen volume divided by the speed of the chemical reaction.

So, you have a certain amount of reactant present in volume, certain kilograms of or certain grams of reactant present in the volume. The speed of the chemical reaction is the rate at which that reactant is getting consumed which is grams of the reactant consumed per second ok. And we are looking at a small volume. So, both the numerator and denominator are divided by the volume. So, it becomes the density inside that volume divided by the speed of the chemical reaction inside that volume ok.

So, that the density divided by the speed of the chemical reaction, which is denoted as omega dot; omega dot is related to the flame speed or the burning velocity which was discussed in the first lecture. Do not worry about the precise functional form of this. We will look at this; we will derive this in a later lecture. What I want you to notice is that the reaction rate is proportional to the flame speed squared.

So, that there is something that is intuitive to us. Faster the flame propagates higher is the reactivity ok. Faster the flame propagates, faster is the reaction and therefore, smaller is the timescale for reaction that alone I would like you to recognize now, the precise relationship we will look at later.

So, now we have an expression for the reaction rate and the reaction time ok. Now, we can estimate the thickness which and you plug in the expression for omega dot into delta going a square root of alpha tr, you will find that delta goes as alpha over the flame speed. This is also something that is intuitive. Faster the burning or faster is the reaction, faster the flame propagates; then, there is the reaction zone.

So, two things I want to reiterate. The reaction rate is higher when the flame speed is higher and the reaction zone thickness is smaller for highest higher flame speeds ok. Yes.

Student: (Refer Time: 16:45).

We are looking at a the example that we are looking at is a premix flame. So, premix flame an important controlling parameter which determines the flame speed of a premix flame is the rate of reaction. So, we are looking at a scenario, where the reaction rates are happening in a finite period of time.

Student: (Refer Time: 17:06) what about the (Refer Time: 17:09).

That infinitely fast chemistry is an assumption that is more relevant for cases where, the fuel in the oxidizer are not pre mixed. So, they are the what becomes more relevant is the time it takes for the fuel and oxidizer to mix and that time is much smaller than the time it takes for the reactions to happen. And therefore, infinitely fast chemistry is relevant there.

In a situation where the reactions are already pre mixed, the there is the mixing time, there is no such thing as mixing time. They are already mixed. What controls the processes is the speed of the chemical reaction. So, it is a finite rate chemistry situation, where it cannot be assumed. If you assume that the reaction rate is infinite, you will also come to the conclusion that the plane speed is infinite, which is not correct. Any other questions? Yeah.

Student: Sir, this flame, the location of the flame that we have been discussing in the flame sequence which essentially involved to the diffusion of the heat speed, the diffusion of the pieces into the same zone.

Correct.

Student: Where are the turbines interaction also contains in the picture.

Yeah.

And the assumption of this delta n over m, where you are taking about the number of molecules entering into the (Refer Time: 18:21) entering into the control volume and exiting. Is that if in the turbulent length scales are in comparison to that, in our assumption is not taking that into account.

Yeah. Anyway, we will have a detailed discussion on this; only point that I want to make here is the turbulent length scale, the smallest turbulent length scale is limited by e.

Student: e molecule?

ah Not really, I mean that the e smallest turbulence scale is limited by the length scale and time scale at which processes become dominated by laminar diffusion based dissipation that is a Kolmogorov scale and that scale is still much larger than the volumes.

Student: Where comes?

Where relative fluctuations can become larger ok. Any other question? Yeah.

Student: (Refer Time: 19:09) here the aluminum (Refer Time: 19:11) centered in the (Refer Time: 19:13) the flame has two zones; one is the actual flame zone, where the emission is very high and (Refer Time: 19:19) is higher and peripheral zone where the reactivity goes down and the relatively the temperature also goes down.

So, how is (Refer Time: 19:24) we are considering homogenously similar elements are across the entire region? So, where the fluctuation is higher or where the drop is drastic to are we not supposed to take more finer elements so.

That is correct.

Student: Capture that.

That is correct. Yeah.

Student: (Refer Time: 19:38).

And that is the reason why we are estimating the thickness of the flame so that the volume that we choose is not much larger than that. So, that.

Student: We are visualizing that.

Yes, the assumption of homogeneity is maintained, I just.

Student: One point (Refer Time: 19:52) its outer zone temperature will be higher, then?

I made a mistake there, yes I. The statement that I made is not correct, where did I make it. Yeah, this statement is not correct. I said that away from the bright blue cone and either say the temperature drops, it is not correct. Only on the inside the temperature drops, outside the temperature will be equilibrium temperature. I should thank you for pointing the doubt. Yeah.

Student: Sir, and one more thing.

Yeah.

Student: For considering the volume that we are going to suppose we are going to model a combustion zone, immediately emphasizing mode on the chemical equilibrium mode. So, that is seriously not have a difference of (Refer Time: 20:33).

Correct.

Student: So, when that comes into future, how are you taking that the assumptions in this, when considering the volume of the control system?

Yeah. So, the reason why we are trying to get an estimate for the size of the or the largest volume that we can pick is so that the state of the temperature of the gases inside and the chemical composition inside can be considered or can be taken to be homogeneous. It means there is no variation space.

Student: (Refer Time: 21:07) will be constant because of higher when we have a higher fluctuation constant.

correct.

Student: Definitely, will have an higher diffusion of masses into the control volume.

That is correct.

Student: Obviously.

That is why we are choosing.

We are choosing.

Student: Will we will not have any chemical immediately.

That is why we choosing. A volume that is such, that the relative fluctuations are smaller and at the same time not too large so that the gradients are significant. Once we get an estimate for the flame thickness you will see the point that I am making, yeah. So, now, with the expression for the reaction rate, we can get a estimate for the thickness of the flame. I have given a few examples of flame speed and flame thickness. The most common example is methane air stoichiometric mixture which has a flame speed of about 40 centimeters per second; for that case the flame thickness is about 250 microns ok.

So, now I would like you to compare this with the volumes at which relative fluctuations becomes significant. It is 0.1 microns. If you pick the volume around the flame, it is only 10 microns. Let us say a cube of size 10 microns, I can reasonably assume that the gradients see the gradients are significant over a length scale of 250 microns. So, I can take a volume that is 10 microns, 10 micron cubes, the gradients will be smaller and the 10 micron is sufficiently large for us to meaningfully different.

Student: (Refer Time: 22:24).

Thermodynamic properties. Correct, yeah. So, it is 250 microns for methane air, even for methane oxygen, it is about 25 microns; hydrogen air is 33 microns; hydrogen oxygen is 5 microns. Therefore, all under all these conditions the flame is sufficiently thick for relative fluctuations to be negligible and continuum assumption is still valid.

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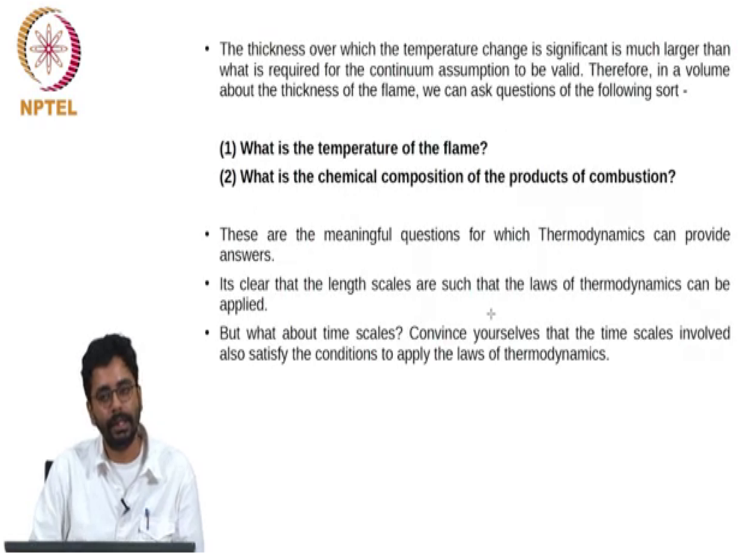

- The thickness over which the temperature change is significant is much larger than what is required for the continuum assumption to be valid. Therefore, in a volume about the thickness of the flame, we can ask questions of the following sort -

(1) What is the temperature of the flame?

(2) What is the chemical composition of the products of combustion?

- These are the meaningful questions for which Thermodynamics can provide answers.
- Its clear that the length scales are such that the laws of thermodynamics can be applied.
- But what about time scales? Convince yourselves that the time scales involved also satisfy the conditions to apply the laws of thermodynamics.

So, the thickness over which the temperature change is significant the temperature change is significant is much larger than what is required for the continuum assumption to be valid. Therefore, in a volume about the thickness of the flame we can ask questions to the following sort; what is the temperature of the flame, what is the chemical composition of the products of combustion ok? And these are the questions that are answered by thermodynamic equilibrium considerations ok.

It is clear that the length scales are such that the laws of thermodynamics can be meaningfully applied. I have not explicitly shown that the timescales also follow the same kind of behavior. I leave it as an as an exercise for you to you know to do something outside of this lecture, yeah.

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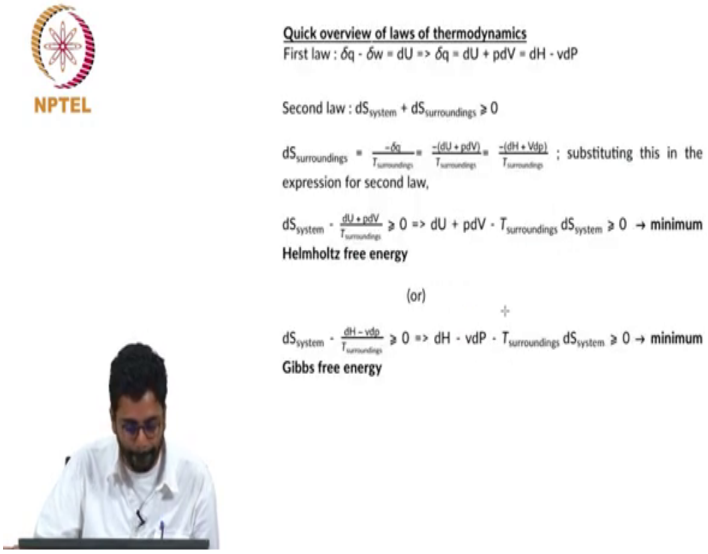

Quick overview of laws of thermodynamics

First law : $\delta q - \delta w = dU \Rightarrow \delta q = dU + pdV = dH - vdP$

Second law : $dS_{system} + dS_{surroundings} \geqslant 0$

$dS_{surroundings} = \frac{-\delta q}{T_{surroundings}} = \frac{-(dU + pdV)}{T_{surroundings}} = \frac{-(dH + Vdp)}{T_{surroundings}}$; substituting this in the expression for second law,

$dS_{system} - \frac{dU + pdV}{T_{surroundings}} \geqslant 0 \Rightarrow dU + pdV - T_{surroundings}\, dS_{system} \geqslant 0 \rightarrow$ **minimum Helmholtz free energy**

(or)

$dS_{system} - \frac{dH - vdp}{T_{surroundings}} \geqslant 0 \Rightarrow dH - vdP - T_{surroundings}\, dS_{system} \geqslant 0 \rightarrow$ **minimum Gibbs free energy**

So, just a quick overview of the laws of thermodynamics; now, that we have convinced ourselves that we can apply the laws of thermodynamics, let us quickly go over the equations. The first law is the law of conservation of energy when applied to a fixed mass undergoing a process, it is simply the difference between the heat transferred and the work done is equal to the change in internal energy of key mass ok, which can be expressed when we only allow for displacement work or pressure volume work the work interaction is pdV. Therefore, the equation can be expressed either as in the form of internal energy or as enthalpy.

Enthalpy is simply internal energy plus pV and the second law is the law of entropy which says that when you have an isolated system, which can be split into a system plus a surrounding. The entropy change for the system plus entropy change for the surrounding will always be greater than or equal to 0 ok. So, now, the entropy change for the surrounding is the heat that is transferred from the system to the surroundings which is negative delta q which is the heat that is lost from the system divided by the temperature of the surroundings this is the definition of entropy which this delta q can now be expressed as using first law as dU plus pdV or dH minus Vdp that is not plus ok.

So when you substitute this back into the expression for delta q, you will end up with an expression of this kind which is dU plus pdV minus temperature of the surrounding and d system is greater than equals 0 and emphasizing this fact that the temperature that we are talking about is the temperature at the surroundings ok. Because when the system undergoes an irreversible process, you we do not actually have a way of defining the temperature for the system is greater than or equal to 0.

This is a minimum Helmholtz free energy statement. Instead of an expression for expression in terms of internal energy, if you use the expression in terms of enthalpy, you will end up with this expression which is dH minus Vdp minus T surrounding dS; d entropy change of the system is greater than or equal to 0 ok.

So what these statements mean is that when you consider a system at constant volume, look at this expression when you consider a system at constant volume you have dU minus T surrounding dS system is greater than or equal to 0. So, when the system is away from equilibrium, this quantity is greater than 0 and when the system approaches equilibrium it reaches 0 ok.

So, similarly here also you have dH minus Vdp, when you consider a system of constant pressure you have dH minus T surrounding dS system dS system is greater than equal to 0 which is a statement of minimum Gibbs free energy. When the system is away from equilibrium the Gibbs free energy is higher and when it is an equilibrium it is lower. Yeah.

Student: Sir, at d system ds of system why are you not using the system temperature, but the surrounding temperature?

You may not always be able to define a system temperature. For example, if you have identified a certain mass as your system, if it undergoes a quasi static process, where it shifts from one equilibrium state to another equilibrium state, where the process is happening slowly. At every point along the process you can identify a temperature pressure and so on.

But, that may not be the case always. When it is undergoing fast process which may happen in fact, in a real system as in the case of the flame that I showed it may so happen that the system goes through a fast change where you cannot actually know the state of the system at every intermediate state. So, you do not know the temperature; you know the temperature at the beginning, you know the temperature at the end, but not in between ok. Yeah.

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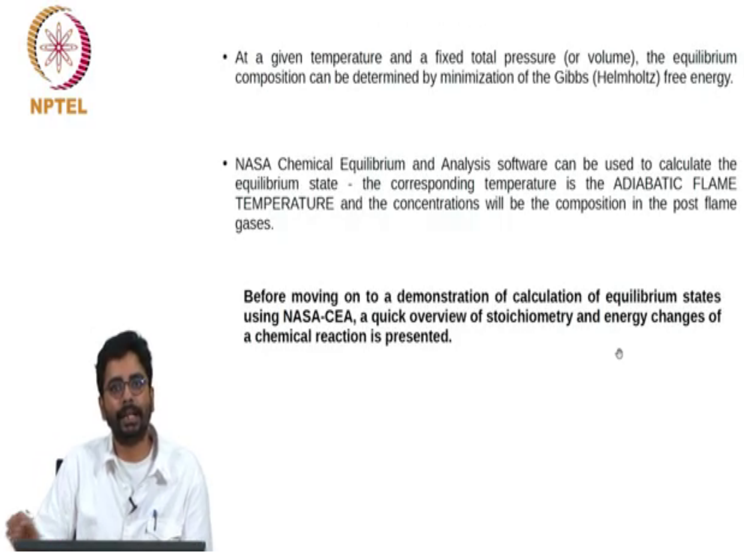

- At a given temperature and a fixed total pressure (or volume), the equilibrium composition can be determined by minimization of the Gibbs (Helmholtz) free energy.
- NASA Chemical Equilibrium and Analysis software can be used to calculate the equilibrium state - the corresponding temperature is the ADIABATIC FLAME TEMPERATURE and the concentrations will be the composition in the post flame gases.

Before moving on to a demonstration of calculation of equilibrium states using NASA-CEA, a quick overview of stoichiometry and energy changes of a chemical reaction is presented.

At a given temperature and a fixed total pressure, the equilibrium composition can be determined by the minimization of the Gibbs free energy under conditions of constant volume. We can determine it by minimizing the Helmholtz free energy. This is essentially what the NASA Chemical Equilibrium and Analysis software does, which I am sure practitioners of you know propulsion design use on a daily basis.

So, this tool can be used to calculate the equilibrium state and the corresponding temperature is called the ADIABATIC FLAME TEMPERATURE. And the concentrations will be the composition in the post flame gases. So, the in the post flame gases the temperature will be equal to the adiabatic flame temperature. Of course, I am assuming that heat loss is negligible; I am assuming that the system is adiabatic.

And, the concentrations will be corresponding to the equilibrium concentration ok. We will have a demonstration of NASA-CEA, at the end of the lecture. But before moving on to a demonstration of calculation of equilibrium states using NASA-CEA, let us take a quick over overview of stoichiometry and energy changes of chemical reactions.

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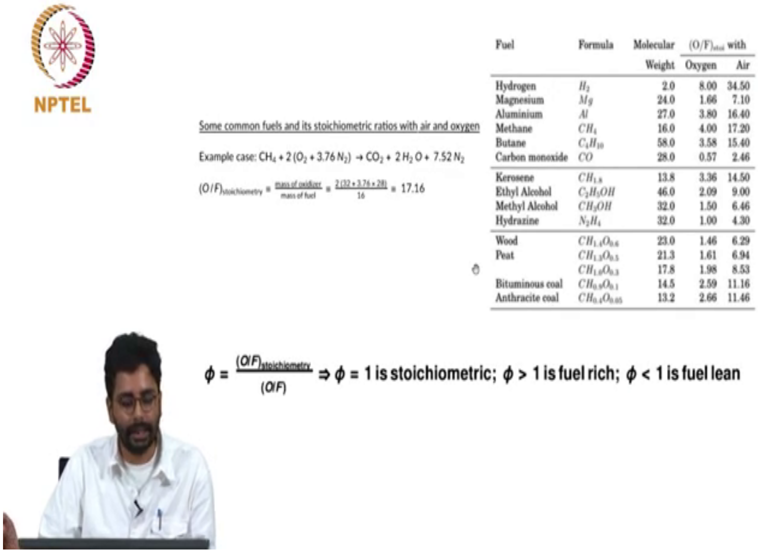

Some common fuels and its stoichiometric ratios with air and oxygen

Example case: $CH_4 + 2(O_2 + 3.76\,N_2) \rightarrow CO_2 + 2\,H_2O + 7.52\,N_2$

$$(O/F)_{stoichiometry} = \frac{\text{mass of oxidizer}}{\text{mass of fuel}} = \frac{2(32 + 3.76 \times 28)}{16} = 17.16$$

Fuel	Formula	Molecular	$(O/F)_{stoi}$ with	
		Weight	Oxygen	Air
Hydrogen	H_2	2.0	8.00	34.50
Magnesium	Mg	24.0	1.66	7.10
Aluminium	Al	27.0	3.80	16.40
Methane	CH_4	16.0	4.00	17.20
Butane	C_4H_{10}	58.0	3.58	15.40
Carbon monoxide	CO	28.0	0.57	2.46
Kerosene	$CH_{1.8}$	13.8	3.36	14.50
Ethyl Alcohol	C_2H_5OH	46.0	2.09	9.00
Methyl Alcohol	CH_3OH	32.0	1.50	6.46
Hydrazine	N_2H_4	32.0	1.00	4.30
Wood	$CH_{1.4}O_{0.6}$	23.0	1.46	6.29
Peat	$CH_{1.3}O_{0.5}$	21.3	1.61	6.94
	$CH_{1.0}O_{0.3}$	17.8	1.98	8.53
Bituminous coal	$CH_{0.9}O_{0.1}$	14.5	2.59	11.16
Anthracite coal	$CH_{0.4}O_{0.05}$	13.2	2.66	11.46

$$\phi = \frac{(O/F)_{stoichiometry}}{(O/F)} \Rightarrow \phi = 1 \text{ is stoichiometric; } \phi > 1 \text{ is fuel rich; } \phi < 1 \text{ is fuel lean}$$

I have taken this simple case to this many of you may be familiar with the stoichiometric oxidizer to fuel ratio is nothing but the ratio of the mass of the oxidizer to the mass of the fuel. The mass of the oxidation should be such that it has enough oxygen to convert all carbon into carbon dioxide and all hydrogen into H2O. I have shown a simple example of methane stoichiometric equation. The oxidizer to fuel ratio for this is 17.2.

In the table on the right hand side, the same thing is shown for a variety of fuels with both oxygen as the oxidizer and air as the oxidation; for hydrogen the oxygen to fuel ratio is 8 and the air to fuel ratio is 34 and so on. Some interesting fuels that I want to want you to notice are some metals, you see that magnesium is listed as a fuel; aluminum is listed as a fuel. These are metals which are high energetic metals which can be oxidized they release a lot of heat are used in rocket fuels, especially in solid rocket motors ok.

Aluminum, magnesium, even boron is considered as a fuel under you know in these rocket propellants ok. Other unusual fuels here which are not hydrocarbon based are one is hydrazine which we saw as a monopropellant that is used in small liquid liquid propulsion systems. In fact, hydrogen can be used both as a monopropellant and as bipropellant. It can be composed on its own releasing energy when sprayed onto a catalyst. It can also be oxidized with additional oxygen ok; because it decomposes into nitrogen and ammonia and hydrogen. It can be further oxidized.

There are other interesting fuels also. Here, you have wood ok, which if you take wood or what we refer to as biomass in general including agricultural residues and variety of forest residues; they all have about the same composition which is approximately $CH_{1.4}O_{0.6}$. So, a kilogram of wood requires about 6, 6 and a half kilograms of air for complete oxidation and other examples here include various forms of decomposed or decomposed wood, let us say peat which eventually becomes cold and anthracite.

So, in this hierarchy of things you start from organic residue which is $CH_{1.4}O_{0.6}$. As you go down the list hydrogen and other volatile components are slowly stripped off and you are left with almost pure carbon when you get to anthracite coal. The oxygen the air to fuel ratio for that is about 12 ok, just again C plus O_2 goes to CO_2, the ratio its air. So, it is O_2 plus 3.76 nitrogen.

So, air; what is written here is 4.76 moles of air which is 1 mole of oxygen plus 3.76 moles of nitrogen. The simplest another way to look at stoichiometry because the numbers are very different for different fuels and normalization that is practice is called the equivalence ratio which is defined as the oxidizer to fuel ratio at stoichiometry divided by the oxidation to fuel ratio, the actual oxidation to fuel ratio.

So, phi equals 1 is stoichiometric; phi greater than 1 is fuel rich and phi less than 1 is fuel lean. This is the most common convention, but you may also find the opposite ok. But this is the most common convention, but one takeaway is that watch out for the definition when you are drawing conclusions.

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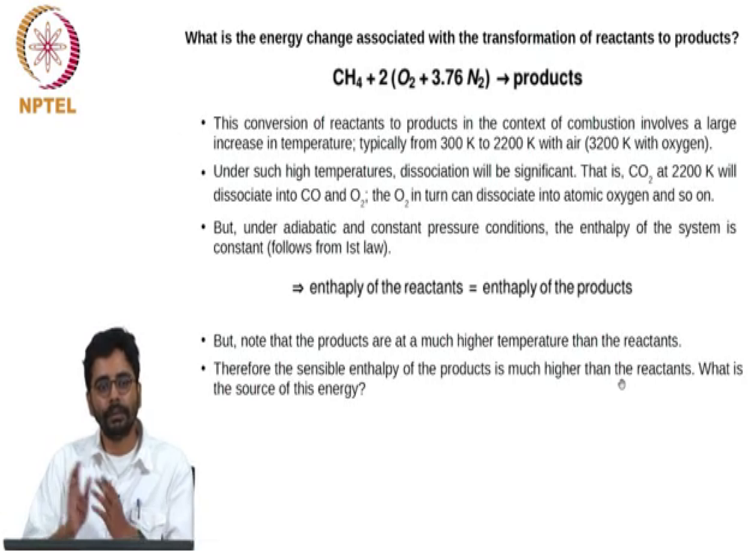

What is the energy change associated with the transformation of reactants to products?

$$CH_4 + 2\,(O_2 + 3.76\,N_2) \rightarrow \text{products}$$

- This conversion of reactants to products in the context of combustion involves a large increase in temperature; typically from 300 K to 2200 K with air (3200 K with oxygen).
- Under such high temperatures, dissociation will be significant. That is, CO_2 at 2200 K will dissociate into CO and O_2; the O_2 in turn can dissociate into atomic oxygen and so on.
- But, under adiabatic and constant pressure conditions, the enthalpy of the system is constant (follows from Ist law).

$\Rightarrow$ enthaply of the reactants = enthaply of the products

- But, note that the products are at a much higher temperature than the reactants.
- Therefore the sensible enthalpy of the products is much higher than the reactants. What is the source of this energy?

So, to apply the laws of thermodynamics, we saw that we need measures of entropy; we need measures of internal energy and so on. So, essentially what we need is a way to keep track or bookkeeping of energy is required ok, to calculate the equilibrium states. So, one question that we need to answer before we can do a calculation is what is the energy change associated with the transformation of reactants to products ok.

So, let us take a simple case which is methane burning in air, I have been careful in not writing the products as CO2 plus 2 H2O. Remember that what we saw in the previous slide is only a statement of stoichiometry ok. So, what we saw here is only a statement of stoichiometry when you actually run the reaction, there is no guarantee that you should get you will get the same products ok, you will get a variety of products.

So, this conversion of reactants to products in the context of conversion involves a large increase in temperature. We know that typically the temperature starting mixture as the temperature of this are room temperature 300 Kelvin’s and increases to about 2200 Kelvin’s with air and to about 3200 Kelvin’s with oxygen under such high temperatures dissociation will be significant. Carbon dioxide will not remain as carbon dioxide at 2200 or for that matter 3200 Kelvin’s. So, we dissociate into carbon monoxide and oxygen.

But, under adiabatic and constant pressure conditions, well its now. So, one thing that we need to keep in mind is that these products can dissociate at high temperatures. So, under adiabatic and constant pressure conditions, we know that the enthalpy of the system should be constant, the application of the first law of thermodynamics.

So, the enthalpy of the reactants must be equal to enthalpy of products, but not that the products are at a much higher temperature than the reactance ok. Therefore, the products have a very large sensible enthalpy and the reactants do not. So, therefore, the sensible enthalpy of the products is much higher than the reactants and the question is what is the source of this energy.

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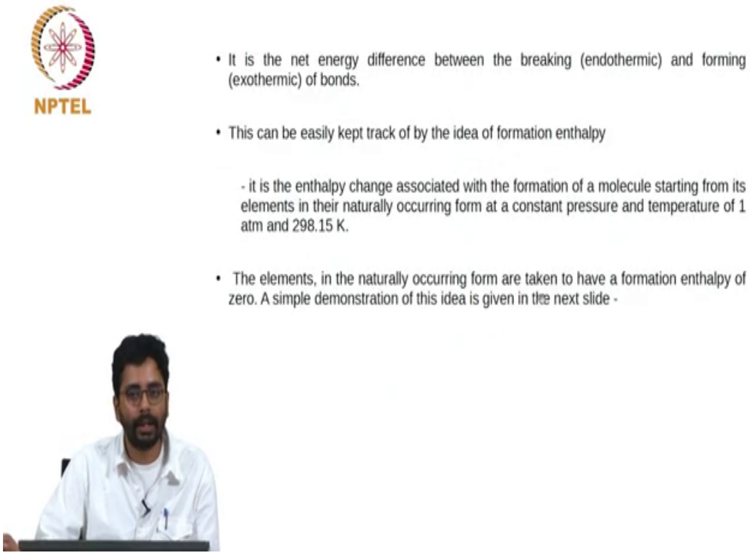

- It is the net energy difference between the breaking (endothermic) and forming (exothermic) of bonds.
- This can be easily kept track of by the idea of formation enthalpy
  - it is the enthalpy change associated with the formation of a molecule starting from its elements in their naturally occurring form at a constant pressure and temperature of 1 atm and 298.15 K.
- The elements, in the naturally occurring form are taken to have a formation enthalpy of zero. A simple demonstration of this idea is given in the next slide -

This is nothing but the net difference between the energy that is required for breaking the bonds between the reactants and the energy that is released when the bonds are formed between the products ok. So, reason why something is a fuel and something is an oxidizer and something is a reactant and something is a product is because the net the total amount of energy that is required to break the bonds between the reactants, will be smaller than the energy that is released because of the formation of the products and that is why these reactions are exothermic. And therefore, have relevance to combustion this.

So, now, we have a variety of oxidizers variety of fuels depending on where you are looking at liquid propulsion systems or gas turbines or solid propellant rockets. So, there are a variety of oxidizers and fuels. So, a simple way to keep track of the idea of this energy associated with reactions is through the idea of formation enthalpy. Formation enthalpy is nothing but the enthalpy change associated with the formation of a molecule, starting from its elements in their naturally occurring form at a constant pressure of 1 atmosphere and a temperature standard temperature of 298.15 Kelvin's ok. So, the elements in the naturally occurring form are taken to have a formation enthalpy of 0 ok. So, this is just a simple way of bookkeeping.

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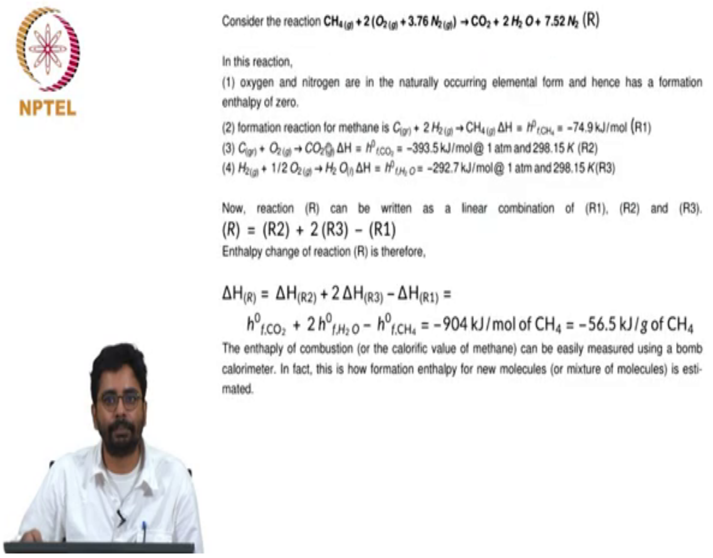

Consider the reaction $CH_{4(g)} + 2(O_{2(g)} + 3.76\,N_{2(g)}) \rightarrow CO_2 + 2\,H_2O + 7.52\,N_2$ (R)

In this reaction,

(1) oxygen and nitrogen are in the naturally occurring elemental form and hence has a formation enthalpy of zero.

(2) formation reaction for methane is $C_{(gr)} + 2\,H_{2(g)} \rightarrow CH_{4(g)}\ \Delta H = h^0_{f,CH_4} = -74.9$ kJ/mol (R1)

(3) $C_{(gr)} + O_{2(g)} \rightarrow CO_{2(g)}\ \Delta H = h^0_{f,CO_2} = -393.5$ kJ/mol@ 1 atm and 298.15 K (R2)

(4) $H_{2(g)} + 1/2\,O_{2(g)} \rightarrow H_2O_{(l)}\ \Delta H = h^0_{f,H_2O} = -292.7$ kJ/mol@ 1 atm and 298.15 K(R3)

Now, reaction (R) can be written as a linear combination of (R1), (R2) and (R3).

(R) = (R2) + 2 (R3) − (R1)

Enthalpy change of reaction (R) is therefore,

$$\Delta H_{(R)} = \Delta H_{(R2)} + 2\,\Delta H_{(R3)} - \Delta H_{(R1)} =$$

$$h^0_{f,CO_2} + 2\,h^0_{f,H_2O} - h^0_{f,CH_4} = -904\ \text{kJ/mol of } CH_4 = -56.5\ \text{kJ}/g \text{ of } CH_4$$

The enthaply of combustion (or the calorific value of methane) can be easily measured using a bomb calorimeter. In fact, this is how formation enthalpy for new molecules (or mixture of molecules) is estimated.

And this will give you a simple demonstration of the idea we will look at the same reaction of course, now I am assuming that the products are these for demonstration. But in realistic cases CO2 H2O will dissociate and you will have a variety of products ok. So, in this reaction oxygen and nitrogen are in the naturally occurring elemental form and hence, it is a formation entropy is 0 according to the definition and formation reaction for methane remember with the definition of formation reaction is that the molecule should be formed from its constituent elements in a naturally occurring form.

So, methane has carbon and hydrogen and naturally occurring form for carbon is carbon and graphitic form and for hydrogen is gaseous hydrogen. So, the reaction is C plus 2 H2O goes to CH 4. The enthalpy change associated with this reaction is a formation enthalpy of methane. You can imagine conducting the reaction in a bomb calorimeter and measuring the enthalpy change.

In fact, what is actually done is that you using a bomb calorimeter, you measure the enthalpy of combustion of methane, from that you can back calculate the enthalpy of formation of methane ok. This is a simple strategy. For example, if you have an exotic fuel which is a new molecule, the simplest way to get formation entropy is to oxidize it completely using air or oxygen, measure the enthalpy of combustion and back calculate the formation enthalpy ok.

Similarly, for carbon dioxide, you can conduct this reaction and get the formation enthalpy and so on for other components. Remember that the naturally occurring form for water is liquid water. So, the enthalpy change associated with the boiling of water must be accounted depending on whether you are interested in combustion products in vapor form or in liquid form. Usually, in the vapor form ok.

The simple idea is that now we the chemical reaction at the top of this page can be expressed as a linear combination of these three reactions. So, the reaction R is reaction 2 plus twice reaction 3 minus reaction 1. Therefore, the enthalpy change for the reaction R is the enthalpy change for reaction 2 plus twice the enthalpy change for reaction 3 minus the enthalpy change for the reaction 2; basic ideas from energy conservation in thermodynamics ok.

So from here, we can calculate the enthalpy of combustion or the enthalpy change for this reaction which is as I have indicated here is negative 56.5 kilojoules per gram. It is negative because it is exothermic. The energy required to break the bonds of methane and oxygen are the is smaller than the energy that is released when the bonds of carbon dioxide and water and other product molecules are formed ok.

Well, this is something that I already mentioned. This is the easiest quantity to measure the enthalpy of combustion. So, what is usually done as you measure the enthalpy of commercial especially when you have a new molecule for which you do not know the formation enthalpy. So, you can you know the enthalpy of combustion, from there you can back calculate the enthalpy for the fuel molecule.