# Fundamentals of Combustion for Propulsion
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## Lecture - 05
## Chemical kinetics, Equilibrium vs rate controlled

Anyway, we will look at will have a demonstration later, but I will just give you one example case results, what is presented in this slide is equilibrium composition for kerosene air mixtures.

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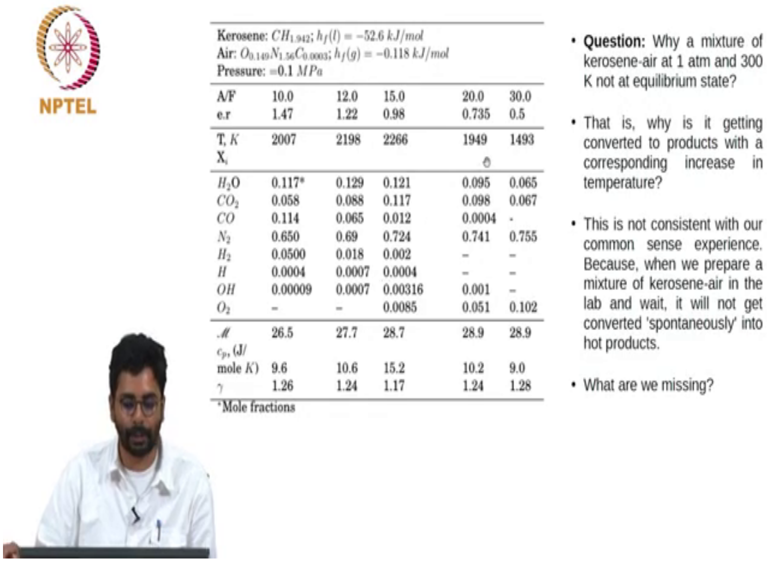

Kerosene: $CH_{1.942}$; $h_f(l) = -52.6\ kJ/mol$
Air: $O_{0.149}N_{1.56}C_{0.0003}$; $h_f(g) = -0.118\ kJ/mol$
Pressure: $=0.1\ MPa$

| A/F | 10.0 | 12.0 | 15.0 | 20.0 | 30.0 |
|---|---|---|---|---|---|
| e.r | 1.47 | 1.22 | 0.98 | 0.735 | 0.5 |
| T, $K$ | 2007 | 2198 | 2266 | 1949 | 1493 |
| $X_i$ | | | | | |
| $H_2O$ | 0.117* | 0.129 | 0.121 | 0.095 | 0.065 |
| $CO_2$ | 0.058 | 0.088 | 0.117 | 0.098 | 0.067 |
| $CO$ | 0.114 | 0.065 | 0.012 | 0.0004 | - |
| $N_2$ | 0.650 | 0.69 | 0.724 | 0.741 | 0.755 |
| $H_2$ | 0.0500 | 0.018 | 0.002 | – | – |
| $H$ | 0.0004 | 0.0007 | 0.0004 | – | – |
| $OH$ | 0.00009 | 0.0007 | 0.00316 | 0.001 | – |
| $O_2$ | – | – | 0.0085 | 0.051 | 0.102 |
| $\mathcal{M}$ | 26.5 | 27.7 | 28.7 | 28.9 | 28.9 |
| $c_p$, (J/ mole $K$) | 9.6 | 10.6 | 15.2 | 10.2 | 9.0 |
| $\gamma$ | 1.26 | 1.24 | 1.17 | 1.24 | 1.28 |

*Mole fractions

- **Question:** Why a mixture of kerosene-air at 1 atm and 300 K not at equilibrium state?
- That is, why is it getting converted to products with a corresponding increase in temperature?
- This is not consistent with our common sense experience. Because, when we prepare a mixture of kerosene-air in the lab and wait, it will not get converted 'spontaneously' into hot products.
- What are we missing?

Kerosene is taken to be for example, this is one case where you can use the enthalpy of combustion to back calculate the formation enthalpy ok. So, what is done here is exactly that.

So, kerosene is a mixture of a large number of hydrocarbons. We and the approximate formula for that is what is given here is CH 2 and the enthalpy of formation is back calculated from the combustion enthalpy and air is also taken to be an equivalent composition that is certain amount of oxygen, nitrogen and carbon.

Remember that you can, you are allowed to do all of these things, because all you need to make sure is that the energy bookkeeping is done correctly ok. You can express the composition in any form it does not have to be H2O or it does not have to be kerosene, need not be considered to be precisely the mixture that it is made up of as long as you get the carbon and the hydrogen correctly and the pressure is taken to be a1 bar.

What is done here is for a variety of air to fuel ratio, temperatures, flame temperature 11 flame temperature is calculated and also the coast flame gas composition is calculated. The important things to note are, we go from an air to fuel ratio of 10 to about 30, stoichiometry is around 15 ok.

So, on the left of 15, the two cases are fuel rich and the to the right of the stoichiometry cases, the two cases are fuel lean. So, equivalence ratio is greater than 1 on the left hand side and less than 1 on the right hand side, it is about 1 in the for the case in the center ok, the third case.

What I want you to notice is for this case, the temperature, the adiabatic flame temperature drops on either side of this stoichiometry and there is about 2270 kelvin such stoichiometry and it drops off on either side and of course, correspondingly you can see that the composition is also consistent with it. There is no oxygen, there is no leftover oxygen when the combustion is rich, there is some oxygen leftover at stoichiometry, because remember that the products are at very high temperatures and therefore, dissociation will happen.

So, carbon dioxide will dissociated to carbon monoxide and oxygen and water vapor can dissociated into hydrogen and oxygen. Therefore, there is a little bit of oxygen that is present at stoichiometry. Of course, the excess oxygen in under lean conditions also can be seen here ok.

Well other thing to notice of course, on the fuel rich side you have fuel species that are left over, hydrogen, atomic hydrogen, molecular hydrogen, and then carbon monoxide are presented in the fuel rich side, but moment you go to the fuel lean side the hydrogen disappears, the carbon monoxide concentration is much-much lower. Recall the NOx versus carbon monoxide and it is relation to equivalent ratio. This is the simplest way to understand it.

Well you also see other things, the relevance of which we will see later. The molecular weight is given the gamma is given, these are relevant for rocket calculations and we will see these aspects, discuss these aspects later. But what I would like to discuss now is, I post a question here, why a mixture of kerosene air at 1 atmosphere and 300 kelvins not at equilibrium state. What I mean by that question is if I start with my initial condition is a stoichiometric mixture of kerosene and air at room temperature and room pressure, you input this data into NASA CEA code and say calculate, you will get this answer. You will get a temperature of 2266 kelvins and composition corresponding to this, but the reason why I am posing this question is this is not consistent with our common sense experience.

When you prepare this mixture for example, in this room and wait for it to spontaneously get converted into high temperature products, it does not happen. So, what is it that we are missing in the equilibrium calculation?

Student: (Refer Time: 04:48) threshold.

Ok, one answer is that these things happen at a finite rate and so?

Student: (Refer Time: 04:58).

Ok. So, the that is a correct, that is a correct point that the rate at 300 kelvins and 1 atmospheres is so small that there is no significant product formation at room temperatures you are saying?

Student: (Refer Time: 05:16) ok it requires some the machinery reaction curve happening you need to separate.

Yeah. So, since the reaction rate at room temperature is so small you need to provide an initial kick. So, if you create a small zone of high temperatures, where a certain amount of product is produced ok, where the temperature has been increased to sufficiently large values ok, for the rate to become significant once a zone of that kind has been created, then the reaction proceeds very fast ok, we know that in a premix case, once you provide an ignition a small flame kernel is created and then the flame kernel propagates through the mixture converting the reactants to products and if you wait for a few seconds, you will have condition that is close to equilibrium after this propagation has ceased ok.

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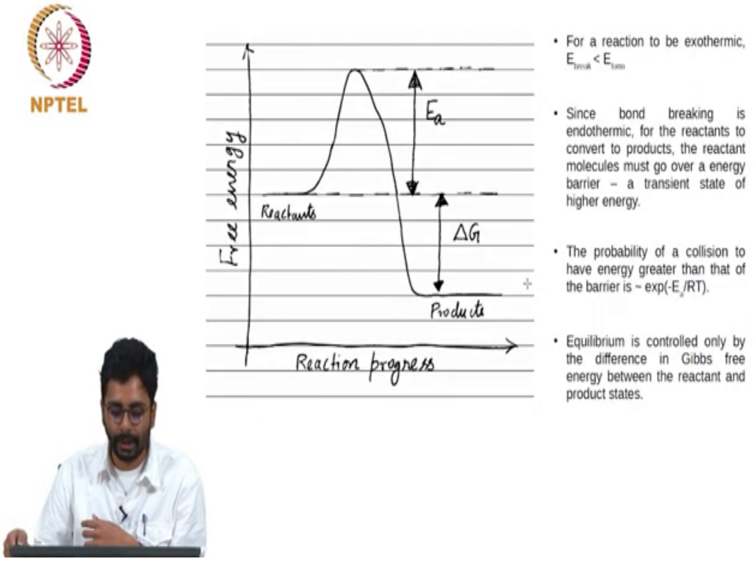

- For a reaction to be exothermic, $E_{break} < E_{form}$
- Since bond breaking is endothermic, for the reactants to convert to products, the reactant molecules must go over a energy barrier – a transient state of higher energy.
- The probability of a collision to have energy greater than that of the barrier is ~ $\exp(-E_a/RT)$.
- Equilibrium is controlled only by the difference in Gibbs free energy between the reactant and product states.

So, points clear ok. That is what I have shown in this simple diagram, what you see on the x axis is the reaction progress, we start with reactants. Reactants are at a high free energy state and the products are at the low free energy state. So, what thermodynamics tells us is that the reactants must spontaneously become products and that is exactly what NASA CEA calculates.

What is missed in the equilibrium calculation is that there is actually a high energy barrier that sort of separates the reactants from the products and for the actual process you should provide a kick or a push that will take the reactants over this, hill and make it products ok.

So, what thermodynamics or what thermodynamic equilibrium calculation sees is only this difference in delta G ok, it does not see the activation energy associated with the activation barrier. So, well this we have already seen for the reaction to be exothermic, the energy required for breaking the bonds must be less than energy required for the formation of the bonds. So, the net reaction is exothermic and the one breaking is endothermic reactions to convert to products.

The reactant molecules must go over an energy barrier or a transients state as it is called it is, because you want breaking process is endothermic and the probability of when you have, when you have created a mixture of this kind a probability that a collision is energetic enough to create sufficient number of transients state radicals or transient state molecules is proportional to exponential minus Ea by RT, the Arrhenius function.

So, the rate is controlled by exponential minus Ea by RT, which is this energy barrier, but equilibrium concerns itself only with this delta G. As long as this delta G is negative, it converts the reactants to products spontaneously. I just want to mention that so, you need ignition systems to cross this energy barrier, but we also have hypergolic combinations ok. So, what happens in hypergolic combinations is that when the fuel and the oxidizer are brought into contact, there are certain energetic condensed phase reactions that can start immediately. They have 0 activation energy and those reactions can start spontaneously, raising the temperature for the rest of the oxidizer and fuel to get converted into product. So, the hypergolic combinations do not require ignition, because of that, but every other combination requires ignition ok.

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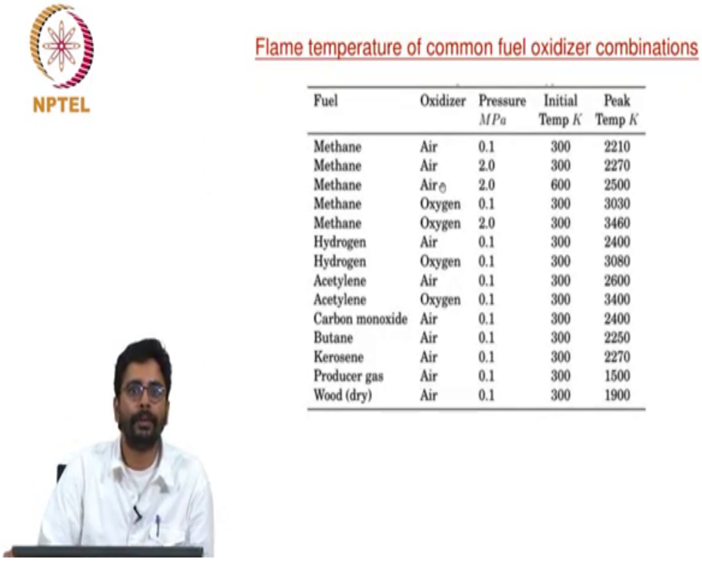

Flame temperature of common fuel oxidizer combinations

| Fuel | Oxidizer | Pressure $MPa$ | Initial Temp $K$ | Peak Temp $K$ |
|---|---|---|---|---|
| Methane | Air | 0.1 | 300 | 2210 |
| Methane | Air | 2.0 | 300 | 2270 |
| Methane | Air | 2.0 | 600 | 2500 |
| Methane | Oxygen | 0.1 | 300 | 3030 |
| Methane | Oxygen | 2.0 | 300 | 3460 |
| Hydrogen | Air | 0.1 | 300 | 2400 |
| Hydrogen | Oxygen | 0.1 | 300 | 3080 |
| Acetylene | Air | 0.1 | 300 | 2600 |
| Acetylene | Oxygen | 0.1 | 300 | 3400 |
| Carbon monoxide | Air | 0.1 | 300 | 2400 |
| Butane | Air | 0.1 | 300 | 2250 |
| Kerosene | Air | 0.1 | 300 | 2270 |
| Producer gas | Air | 0.1 | 300 | 1500 |
| Wood (dry) | Air | 0.1 | 300 | 1900 |

Again more cases here what is shown is, two things are shown one is effect of initial temperature and also effect of initial pressure ok. Let us ok, I cannot see a case where the pressure is 1 bar and the initial temperature is 600 ok. Let us not worry about it, let us look at these two cases; methane air, the pressure is for both these cases is 20 bar 2 mega Pascal’s here, the initial temperature is 300, here the initial temperature the 600 of course, the enthalpy that is used to raise the temperature of the initial reactant is available for raising the temperature of the products also. So, some of this gets reflected in the final temperature increase and well of course, the same thing is shown for methane oxygen combinational also, I do not want to discuss it in detail. The point that I want to make is that of course, raising the temperature of the reactants will increase the adiabatic flame temperature.

The other point which, I want you to think about is, at the same initial temperature increasing the pressure will increase the final adiabatic temperature till some level of pressure that is because the extent of dissociation decreases with increase in pressure.

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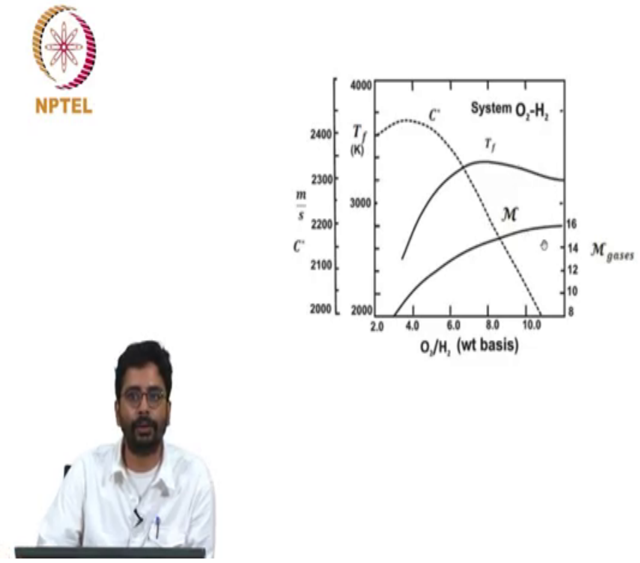

Just again, few more cases of equilibrium composition, this is for this I wanted to include, because I made a point here, saying that the temperature is maximum at stoichiometric conditions, this need not always be the case. One example is oxygen hydrogen system, where maximum temperature occurs at rich conditions, sufficiently rich conditions.

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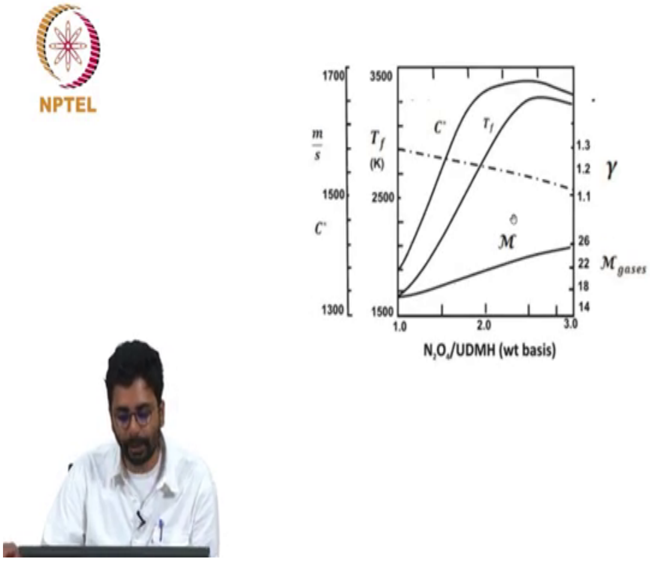

Again, one more case of hypergolic combination of propellants are nitrogen tetroxide and unsymmetrical dimethyl hydrazine, these are just, I wanted to show the trends in flame temperature molecular weight and what is called the characteristic velocity which we will discuss later at right now, I will suggest that you look only at the way flame temperature changes with the key oxidizer to fuel ratio ok.

In different you know communities look at measures of oxidation to fuel ratio in different ways. In combustion literature is usually equivalence ratio, but if you talk to liquid propellant rocket person you will talk about mixture ratio and if you talk to a solid propellant man he will say you know solid loading or the amount of Ap that is present in the propellant, but they are all essentially the same measure you can calculate one from the other yeah.

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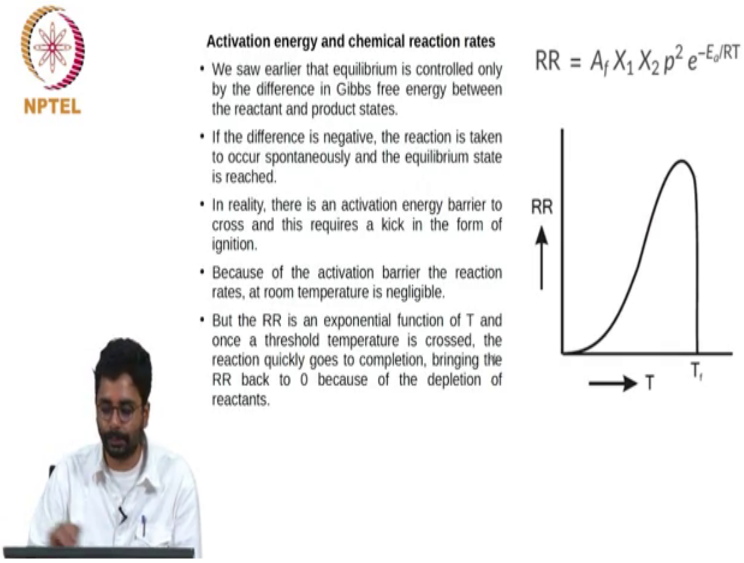

**Activation energy and chemical reaction rates**

- We saw earlier that equilibrium is controlled only by the difference in Gibbs free energy between the reactant and product states.
- If the difference is negative, the reaction is taken to occur spontaneously and the equilibrium state is reached.
- In reality, there is an activation energy barrier to cross and this requires a kick in the form of ignition.
- Because of the activation barrier the reaction rates, at room temperature is negligible.
- But the RR is an exponential function of T and once a threshold temperature is crossed, the reaction quickly goes to completion, bringing the RR back to 0 because of the depletion of reactants.

$$RR = A_f X_1 X_2 p^2 e^{-E_a/RT}$$

So, will this we have already discussed, I will just formalize the notion of reaction rate and Arrhenius parameters. So, we saw earlier that equilibrium is controlled only by the difference in Gibbs free energy between the reactant and product states.

If the difference is negative then products have a lower Gibbs free energy and the reactants reaction is taken to occurs spontaneously and equilibrium state is achieved, but in reality there is an activation barrier to cross this and this requires a kick in the form of ignition and, because of the activation barrier, the reaction rates at room temperature are negligible what you see here is a plot of reaction rate versus temperature, the reaction rate is almost 0 at low temperatures and it becomes significant only at certain temperature and that temperature depends on what fuel oxidizer mixture you are dealing with. Therefore, the reaction rate exponentially increases with temperature.

So, once you cross that threshold temperature the reaction rate increases exponentially, but also remember that in the process the reactants are consumed. So, the reaction rate is proportional to the concentration of the react product of the concentration of the reactants and a temperature function which is the Arrhenius function. So, as the temperature increases, this term the exponential term will go up very fast, but in the process you are also consuming the reactants and therefore, at some point you will reach a stage where all the reactions are consumer reaction rate will drop to 0 ok.

So, this state is close to the equilibrium state, when all the reactants have been consume consumed, converted into products, temperature is increased and an equilibrium state has been achieved and the reaction rate goes to 0 at equilibrium state and that reaction rate goes to 0 at equilibrium state well.

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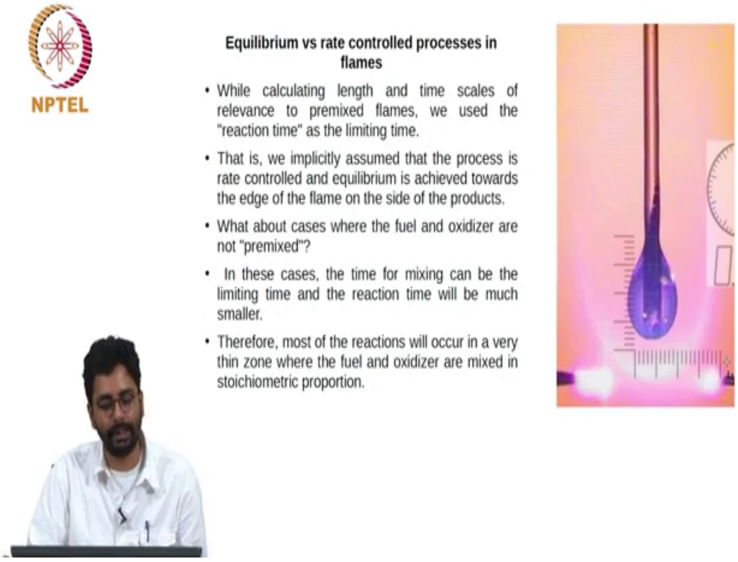

**Equilibrium vs rate controlled processes in flames**

- While calculating length and time scales of relevance to premixed flames, we used the "reaction time" as the limiting time.
- That is, we implicitly assumed that the process is rate controlled and equilibrium is achieved towards the edge of the flame on the side of the products.
- What about cases where the fuel and oxidizer are not "premixed"?
- In these cases, the time for mixing can be the limiting time and the reaction time will be much smaller.
- Therefore, most of the reactions will occur in a very thin zone where the fuel and oxidizer are mixed in stoichiometric proportion.

Any questions at this point before, I get started with this, I think I have a couple of slides before we close this lecture and move to the NASA CEA demonstration, but if you have a question, I can answer now.

Student: (Sir, how does the initial pressure increases the endothermic (Refer Time: 13:55) adiabatic flame temperature.

Sorry?

Student: How?

How the initial pressure increases? So, the extent of dissociation for example, if you consider the dissociation of carbon dioxide, if you fix the temperature at let us say at 2000 kelvins, at 1 atmosphere the extent of the dissociation of carbon dioxide will be much more than what it is at 5 atmospheres and the dissociation reactions are endothermic, they will consume energy, and bring down the temperature.

So, once the extent of dissociation decreases as the pressure increases the flame temperature increases. What I want you to think about is why does the extent of dissociation I mean decrease with increase in pressure and it is something that I leave it as an exercise for you to think about. Yeah, any other questions, no? Shall we move on? Yeah.

Student: Can we move 4 slides back?

Sure.

Student: This why this (Refer Time: 14:53).

Yeah, that is what I so, if you in the liquid rocket propellant literature, the variable that is used to you know specify the fuel oxidizer ratio is what is called the mixture ratio. It is the mass flow rate of the oxidizer divided by the mass period of the fuel. So, here this is a hyperbolic combination, where the oxidizer is nitrogen $N_2O_4$ and the fuel is actually UDMH unsymmetrical dimethyl hydrazine. So, this is the oxidation this is the fuel. So, the way the equivalence ratio is expressed, is as the ratio of mass of the oxidation to the mass of the fuel. So, this is the ratio of mass of the oxidation and mass of the fuel, any other questions?

I will just spend about 10 minutes discussing this. So, we have discussed equilibrium, but we have also seen that there are some aspects of combustion, which are dependent on the rate of the chemical reactions ok. So, when looking or when analyzing flames it is important to identify the dominant process. Sometimes a dominant process is mixing and equilibration, sometimes the dominant process is chemical reaction.

So, what I am referring to as equilibrium versus rate control processes is equilibrium refers to processes, where the chemical reaction rates can be considered to be much-much higher than every other process ok. So, the there is sufficient time available for the reactions to go the equilibrium ok. So, the rate of those processes are not controlled by chemical reaction rates, because the chemical reaction rates are much larger than the other processes, it will be controlled by the slowest of all the processes that happen ok.

One example of such a case is what is shown here, what you see here is an ethanol droplet suspended by a quartz rod, ignited with a spark, you can see a thin bluish color flame that is surrounding the droplet. It is not prominently visible, because the picture has been taken with backlight so that we can simultaneously see the flame as well as the droplet.

So, in the absence of the black in the absence of the backlight, you will actually see a prominent blue flame here ok. This flame is formed by the reaction between ethanol vapors are coming off from the surface of the droplet which come off mixed with the air from the surrounding and react and form a flame. So, this is a non pre mixed situation. This is not a premix situation, this is a non premix situation, where ethanol vapors come from inside of the flame, oxidizer diffusers from outside of the flame, both diffuse towards the towards the flame mix and react.

In fact, they move towards each other mix and react and the point of maximum reaction is the flame ok. So, here is a example here is an example where for instance, this process or the time it would take for the droplet to completely vapor is what controls the process here. So, the limiting timescale is the droplet vaporization rate and not the rate of chemical reaction ok.

So, this is a case where, if you for example, assume that the reaction rate is controlling, the timescales that you would estimate will be much smaller than what in reality it is ok. So, what happens here is since, the reaction rates are much-much higher, the vapors the vapors of ethanol and oxygen from the surrounding air have a lot of time to equilibrate ok. So, the reaction rates are much larger. So, there is a lot of time available for the reactions to go to completion go to a point where the reaction rate or the net reaction rate is 0 ok.

So, in fact, the state around the flame will be close to what you see here. The temperature will be close to the adiabatic flame temperature and the reaction rate will be 0 that is these observations are worked as summarized here, I will go through it just to make sure that you conveyed all the points.

I conveniently chose a premix flame, where the reaction rate is controlling to calculate the land scales, to justify the continuum assumption and the assumption of thermodynamic equilibrium. So, while calculating length and timescales of relevance to premix names.

We use the reaction time as a limiting time, I picked an example where reaction time is a limiting time that is we implicitly assume that the process is rate control and equilibrium is achieved towards the edge of the flame on the side of two products, but of course, there are there are a lot of cases in reality where the reactants are not pre mixed. For example, the droplet flame that you see on the right. In these cases the time for mixing can be the limiting time and the reaction time will be much smaller.

In fact, in this case the time for mixing is also not the limiting time, it is their operation time that is the limiting time. Therefore, most of the reactions will occur in a very thin zone. It is not that easy to define thickness your with reactions are infinitely fast reaction 0 is necessarily has a thickness of 0. So, therefore, most of the reactions will occur in a very thin zone, where the fuel and oxidizer and mixed in stoichiometric proportion

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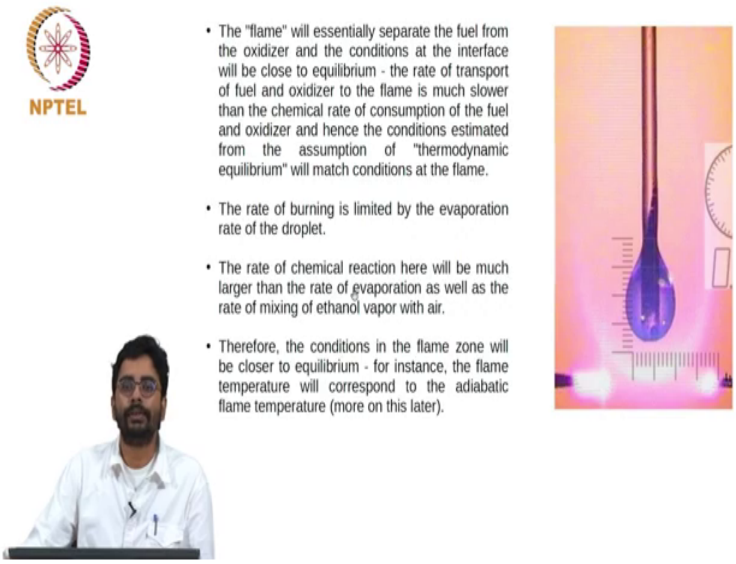

- The "flame" will essentially separate the fuel from the oxidizer and the conditions at the interface will be close to equilibrium - the rate of transport of fuel and oxidizer to the flame is much slower than the chemical rate of consumption of the fuel and oxidizer and hence the conditions estimated from the assumption of "thermodynamic equilibrium" will match conditions at the flame.
- The rate of burning is limited by the evaporation rate of the droplet.
- The rate of chemical reaction here will be much larger than the rate of evaporation as well as the rate of mixing of ethanol vapor with air.
- Therefore, the conditions in the flame zone will be closer to equilibrium - for instance, the flame temperature will correspond to the adiabatic flame temperature (more on this later).

So, the flame will essentially separate the fuel from the oxidation. In the premix case the flame separated the reactants from the products, the premix reactants from the products. Here, it separates the fuel from the oxidizer and the conditions of the interface will be close to equilibrium.

Rate of transport a fuel and oxidizer to the flame is much slower than the chemical rate of consumption of the fuel and oxidizer and hence, the conditions estimated from the assumption of thermodynamic equilibrium will match conditions at the flame. So, you can, as far as the chemical state is concerned and the are as far as the thermodynamic state is concerned. You can assume equilibrium, what you need to accurately account for is the time it takes for the mixing of the reactants to happen or mixing of the fuel with the oxidizer to happen.

So, the rate of burning is limited by the evaporation rate of the droplet. For the example that is shown here, the rate of chemical reaction here, will be much larger than the rate of evaporation as well as the rate of mixing of ethanol vapor with air. Therefore, the conditions, I am just repeating this point, the conditions in the flame zone will be closer to equilibrium. For instance, the flame temperature will correspond to the adiabatic flame temperature., I think I will stop here, I have spoken for about an hour I will take some questions, if you have yeah, yes.

Student: (Refer Time: 21:52) you showed the equation for reaction rate sir.

Yeah.

Student: Then how we will (Refer Time: 21:58).

We will discuss that when in the next lecture. it is, generally, it is difficult to measure reaction rates, but there are simple ways by which we can get an estimate of the overall or the order of the reaction rate by quantities that are much that are easier to measure compared to reaction rate. For example, I showed an equation for the reaction rate, which I used for calculating the, look at this equation omega dot goes to Cp over k rho u Su square.

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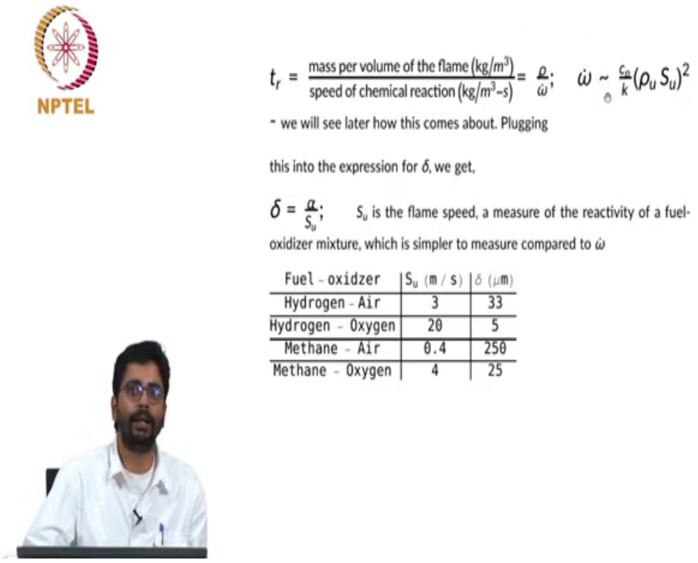

$$t_r = \frac{\text{mass per volume of the flame } (kg/m^3)}{\text{speed of chemical reaction } (kg/m^3\text{–}s)} = \frac{\rho}{\dot{\omega}}; \quad \dot{\omega} \sim \frac{c_p}{k}(\rho_u S_u)^2$$

- we will see later how this comes about. Plugging

this into the expression for $\delta$, 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) | $\delta$ ($\mu$m) |
|---|---|---|
| Hydrogen - Air | 3 | 33 |
| Hydrogen - Oxygen | 20 | 5 |
| Methane - Air | 0.4 | 250 |
| Methane - Oxygen | 4 | 25 |

So, omega dot is a measure of sort of an average reaction rate over the flame thickness, which is not very easy not easy to measure, but what is easy to measure is the flame speed. So, once you know the flame speed, you can relate it to the react, reaction and the reactivity.

You will not get the exact magnitude, you will not get information about all the complicated pathways through which the actual conventional reactants to products happen, but there are situations where that information is not required. For example, but there are situations, which one example of which is the combustion process that happens over the surface of a composite solid propellant.

This kind of strategy or this strategy for estimating reaction rates from flame speeds, the numbers that you get are good enough to actually get, good enough to actually create a theoretical framework for calculating or predicting the burn rate of composite solid propellant ok.

There are a large number of parameters involved, all that you need to make sure is that the set of parameters are internally consistent. Once, you ensure that the corrections match with the experimental results, but the reaction rate is only an average reaction rate estimated from relationship of state. We will discuss this in some detail later today and tomorrow in the context of solid propellants. Any other questions, yeah.

Student: You told like (Refer Time: 24:06) aluminum also used as.

Yes.

Student: So, how we use these as a fuel like we mix with some other fuel sir like.

Yeah, in the case of solid propellants for example, if you once one example is the solid rocket boosters that are used in the PSLV launch vehicle, it is called an S 200 booster that has a propellant, which consists of ammonium perchlorate mixtures of ammonium perchlorate HTPB, which is a kind of rubbery like material which acts as a hydrocarbon fuel and aluminum.

So, all these are mixed and made into a solid block, which can then burn and the what generally happens is the ammonium perchlorate is the oxidizer, HTPB and aluminum are fuel. So, the ammonium perchlorate and HTPB reacts and form commercial products and aluminum can be oxidized by the combustion products of AP and HTPB. For example, aluminum can be oxidized by water vapor, aluminum can be oxidized by carbon dioxide also.

So, those exothermic reactions add more enthalpy to the hot gases that flow and that enthalpy increase can contribute to a better performance. So, the way the aluminum is incorporated into the propellant is by mixing it and making it into a solid blocks and if I remember right, magnesium is used in astra propellant for example. So, these are all mixed and made into a solid block which is burnt inside the combustion chamber.