Fundamentals of Combustion

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Lecture - 11

First law and Second law of thermodynamics applied to combustion - Part 3

Calculation of Flame Temperature

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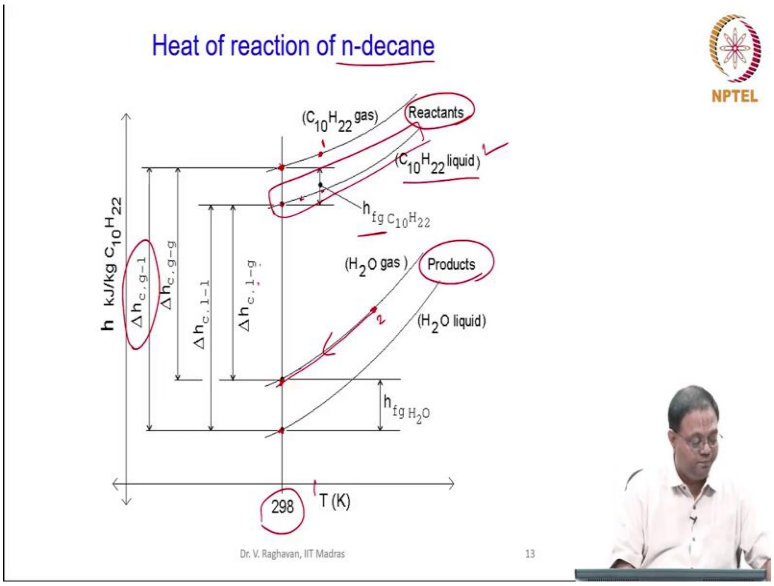

Heat of reaction of n-decane

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Now, one more graph I am showing here is how the heat of reaction is defined. I have specifically taking a fuel called n-decane here, because n-decane exists as a liquid fuel at atmospheric condition.

Now, reactants are at higher energy level. So, the curves for the reactant mixtures appear here. The enthalpy curves for the products appear at the bottom as the function of temperature. You can see that the reactants are at higher energy level or higher enthalpy level than the products.

If you see the enthalpy of the reactants you can calculate it in two ways because the fuel can be in liquid or vapor state. You can vaporize and supply to the combustion chamber or you can supply that liquid directly. Based upon what you supply, that will give the curve in the bottom. When the reactant has a liquid fuel in it you get a curve in the bottom.

Now, first of all this has to be heated up. You have to supply the enthalpy of vaporisation of the fuel h_{fg}, to this liquid, so that it converts into vapor.

This at a particular pressure, whatever will be the pressure of the operation based upon that you calculate the h_{fg} and supply that heat. So, you get the gas mixture. Now this curve corresponds to the enthalpy variation where the reactant, the fuel in the reactant mixture is in vapor state or gas state. Then products are formed. Now, please understand that the reactants can be at 298 Kelvin or any other temperature. For example, I can also supply reactant at 400 Kelvin or any other temperature.

So, liquid reactant at 400 Kelvin can be supplied and products are formed. Products may not go to 298 Kelvin, products can also exist at some other temperature. So, wherever I put these points, this is state 1 and this is state 2.

The difference between the state 1 and state 2 will be the heat of combustion. You can see then based upon the temperature I can fix the states. Now, standard condition is this vertical line at 298 Kelvin.

Whatever be the reactant mixture, whether it has liquid fuel or gaseous fuel, I get these two points. Similarly, when I form the products I get product with gaseous H_2O or liquid H_2O, that will give you these two points.

Now, the heat of reaction will vary. So, when I say Δh_c or heat of reaction, heat of combustion is negative of that. L to g means fuel is in liquid state and water vapor in the product is in gas state. So, that will be these two lines.

When I say this where the liquid fuel is supplied, here you can see that the product has gaseous H_2O.

Now, what happens is you get the maximum energy level for the reactant mixture when the fuel is in gaseous state. When the water vapour is in the liquid state in the products you get the minimum energy level for the product mixture. So, this corresponds to the maximum heat which can be extracted.

So, based upon the phase of the fuel in the reactant or water in the products we will get different values of this. This is standard heat of reaction. Standard heat of reaction also will vary based upon this.

Now, we cannot have combustion reaction in liquid state. So, you can almost ignore this particular line, but taking this line, this is the state 1 for us. Somehow you supply heat, so that the fuel in the reactants are in the gaseous state. Now, reaction is complete.

When you reach this state, you get what is called lower heating value because the water is in vapor state, go to this state you get higher heating value because the water is in liquid state. This is the heat calculation.

So, by using first law we can do this, but we need to calculate the absolute enthalpy of each species which is sum of the enthalpy of formation and the sensible enthalpy.

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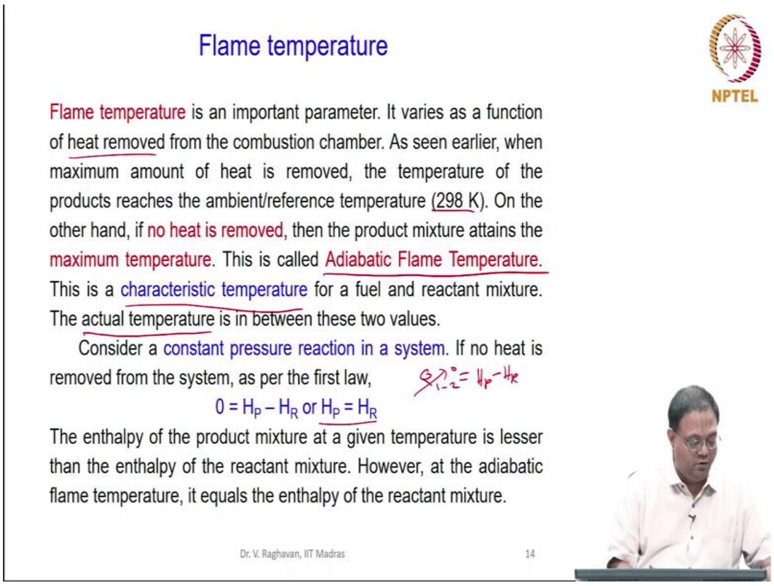

Flame temperature

Flame temperature is an important parameter. It varies as a function of heat removed from the combustion chamber. As seen earlier, when maximum amount of heat is removed, the temperature of the products reaches the ambient/reference temperature (298 K). On the other hand, if no heat is removed, then the product mixture attains the maximum temperature. This is called Adiabatic Flame Temperature. This is a characteristic temperature for a fuel and reactant mixture. The actual temperature is in between these two values.

Consider a constant pressure reaction in a system. If no heat is removed from the system, as per the first law, $\cancel{Q_{1-2}}^{0} = H_P - H_R$

$$0 = H_P - H_R \text{ or } H_P = H_R$$

The enthalpy of the product mixture at a given temperature is lesser than the enthalpy of the reactant mixture. However, at the adiabatic flame temperature, it equals the enthalpy of the reactant mixture.

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Now, second calculation what we try to do here is called temperature calculations. If you see this figure again I told you that I can start from any state here, say some pre-heated reactant. Reactant maybe at a higher temperature and products, I need not cool it to 298 K always, I can cool it to any temperature. For example, it may not be at the reactant temperature of 400 K here, it may be at 1000 or 1500 K. So, these states are fixed.

What is the temperature? This temperature and heat transfer are mingled with each other, when you carry out maximum heat transfer what happens is you get the minimum product temperature. For example, I start from this temperature 298 K and I form products. Products are at any other temperature, so some temperature like this say state 2. So, this may be the actual reaction. But I cool the products and reach this state. Now, we can see that I get more heat, but temperature has reduced.

The flame temperature is an important parameter, we cannot always cool it to 298 K, as I told you when you cool a combustion chamber the combustion reaction may cease to exist. There should be some heat which will be available to sustain the reactions and it will be quenched if you cool the combustion chamber.

Slightly away from the important combustion zone only cooling can be done. Even in a furnace, the boiler is set up at a particular height from the furnace you do not put the boiler where the heat exchanging tubes are present in the primary combustion zone, because that will quench the reactions. We should not quench the reaction you have to allow the reaction to take place. So, the flame temperature is important parameter.

For example, if I try to cool it you can reduce the temperature as much as you want. But if you do not cool it at all, what is the maximum temperature that can be reached? So, these are the two extremes what we have. So, flame temperature is an important parameter which varies with the heat removal from the combustion chamber.

So, when you cool the products to 298 K, you get the maximum amount of heat. On the other hand, if no heat is removed then temperature attains the maximum value. When no heat is removed the condition is called adiabatic.

And when you reach the condition of no heat removal then you get the temperature which is defined as adiabatic flame temperature. The adiabatic flame temperature is the temperature attained by the products when there is no heat removal from the combustion chamber.

This is again a characteristic temperature of the fuel and reactant mixture based upon the conditions. Now, a lowest temperature is attained when you do all the heat extraction that will be the reference temperature, 298 K.

Maximum temperature is the adiabatic temperature where we do not do any heat removal at all and in between these two will be the actual temperature. Normally we do not exert all the heat or we do not make it completely adiabatic.

Now, you can again use the first law to calculate this. First law for a constant pressure system, Q_{1-2}, was equal to H_P - H_R. I can see that Q_{1-2}, if it is 0, that is adiabatic, the $H_P = H_R$.

The enthalpy of product mixture at a given temperature, any temperature if you take, this is the temperature line any vertical line I draw here, I always see that the reactant mixture are at higher energy level than the product. At any given temperature the enthalpy of the reactant mixture will be higher than that of the products.

The enthalpy of product mixture will be lesser than the enthalpy of the reactant mixture. However, at the adiabatic flame temperature it equals the reactant that is $H_P = H_R$.

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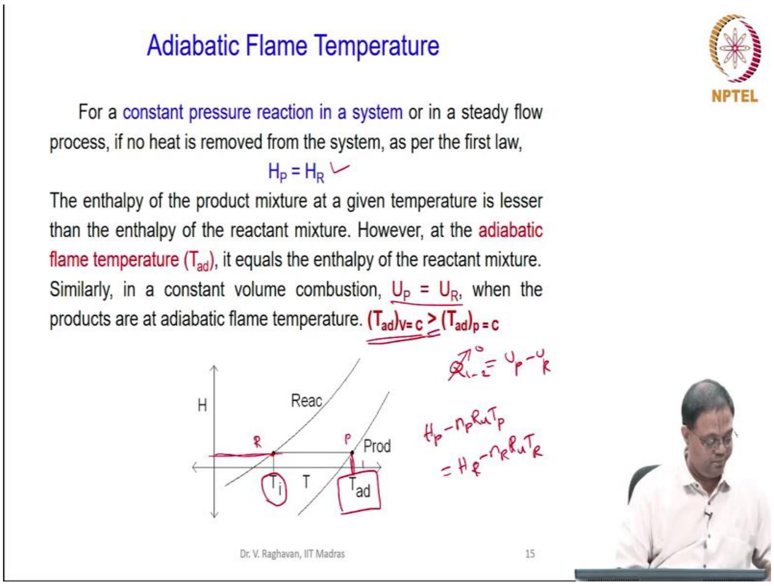

Adiabatic Flame Temperature

For a constant pressure reaction in a system or in a steady flow process, if no heat is removed from the system, as per the first law,

$$H_P = H_R$$

The enthalpy of the product mixture at a given temperature is lesser than the enthalpy of the reactant mixture. However, at the adiabatic flame temperature (T_{ad}), it equals the enthalpy of the reactant mixture. Similarly, in a constant volume combustion, $\underline{U_P = U_R}$, when the products are at adiabatic flame temperature. $\underline{(T_{ad})_{V=C}} > (T_{ad})_{p=C}$

$$\overset{0}{\cancel{Q_{1-2}}} = U_P - U_R$$

$$H_P - n_P R_u T_P = H_R - n_R R_u T_R$$

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So, that is what I have shown here you can see enthalpy versus temperature, reactant curve and the product curves are appearing like this. If you take for example, like this any temperature this is the product enthalpy and it is lesser than the reactant enthalpy. But this is the initial temperature of the reactant, so state 1 is here or the reactant state.

Now, reaction completes and products are formed. The adiabatic flame temperature is defined as when the enthalpy of the reactant R is equal to that of P. What is the temperature at which enthalpy of the product matches the enthalpy of the reactant?

That will be termed as the adiabatic flame temperature. So, in a constant pressure system, $H_P = H_R$. So, products need very high temperature to match the enthalpy of the reactant mixture.

Now, if you go to constant volume system, then first law is $Q_{1-2} = U_P - U_R$, and if adiabatic, $Q_{1-2} = 0$. So, $U_P = U_R$.

Now, we can estimate again $H_P - n_P R_U T_P = U_P$. We can equate this to H_R. We can write this as $H_P - n_P R_U T_P = H_R - n_R R_U T_R$.

Now, we can note from this that, since in a constant volume process there is no dissipation of energy as work you can see that the adiabatic flame temperature, calculated for a constant volume, V = C, is greater than the adiabatic flame temperature calculated when the pressure is held constant in the system.

Because of the fact that there is no like dissipation of energy in terms of work. If you take the constant pressure process, the dissipation of energy occurs due to displacement work. Here, the entire energy is used only to increase the temperature of the products. So, the adiabatic flame temperature at a constant volume combustion is higher than that at constant pressure.

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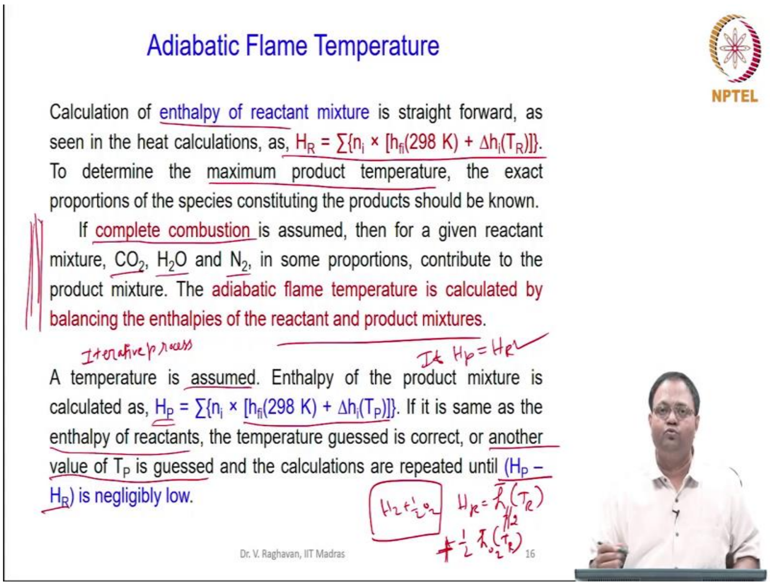

Adiabatic Flame Temperature

Calculation of enthalpy of reactant mixture is straight forward, as seen in the heat calculations, as, $H_R = \sum\{n_i \times [h_{fi}(298\ K) + \Delta h_i(T_R)]\}$. To determine the maximum product temperature, the exact proportions of the species constituting the products should be known.

If complete combustion is assumed, then for a given reactant mixture, CO_2, H_2O and N_2, in some proportions, contribute to the product mixture. The adiabatic flame temperature is calculated by balancing the enthalpies of the reactant and product mixtures.

Iterative process

If $H_P = H_R$

A temperature is assumed. Enthalpy of the product mixture is calculated as, $H_P = \sum\{n_i \times [h_{fi}(298\ K) + \Delta h_i(T_P)]\}$. If it is same as the enthalpy of reactants, the temperature guessed is correct, or another value of T_P is guessed and the calculations are repeated until $(H_P - H_R)$ is negligibly low.

$\boxed{H_2 + \frac{1}{2}O_2}$ $H_R = \bar{h}_{H_2}(T_R) + \frac{1}{2}\bar{h}_{O_2}(T_R)$

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Now, calculation of enthalpy of reactant mixture is straightforward, because you know what are the fuel and oxygen species you are putting in. For example, if we take say H_2 + 1/2 O_2, I know the reactants are fixed. One mole of H_2 and 1/2 moles of O_2 is here.

So, I can calculate the enthalpy of reactant mixture very easily. For example, the H_R for this will be equal to $\bar{H}_{H_2}$ at any temperature. I put a overhead bar here into 1. I am not putting one plus half times $\bar{H}_{O_2}$ at the reactant temperature, 298 K, because its 0. H_2 and O_2 are basic elements, so this will be 0. $H_R = 0$. If the T_R is more than 298 K, then you have to add the sensible enthalpies.

So, by this you know there is no complication because we are supplying the reactants and reactant enthalpy can be calculated easily.

Now, to calculate the adiabatic flame temperature, which is the maximum product temperature without any heat transfer, exact proportions of the product should be known. Species which is contributed to the product should be known to us.

For example, how many moles of CO_2 whether it has dissociated to form CO, we do not know that. If we do not know that then it is not easy to do the calculation of the temperature.

So, now, in the first step let us assume complete combustion takes place and the products of hydrocarbon fuel such as CO_2, H_2O and N_2 in the air remains in the product mixture.

So, that is what we get. Now, we know based upon the carbon and the hydrogen balances and amount of air supplied, it may not be stoichiometric, if it is stoichiometric N_2 will be present in the products. If it is excess air oxygen also can be present here.

So, when I say complete combustion, I just balanced the reactants and only assume CO_2 is the product generated from carbon atoms and H_2O is product generated from the hydrogen molecule. But there is no other intermediate species or dissociated species like CO, H_2.

That is the main assumption I am making here as the first step, because when reactant species are known to me H_R calculation is straightforward. Calculation of product enthalpy requires the composition.

How will you do that? So, we do not know how to do that. So, let us first of all assume there is a complete combustion. This is not true that is what I am trying to prove.

So, in this case, CO_2 and H_2O are the only product I am considering which are formed from the reaction. Nitrogen of course is treated as inert and oxygen, if it exists that will appear. But please understand that I cannot supply air which is less than stoichiometry because then this formation will not be complete.

Now, in this scenario itself we will see that you cannot calculate the adiabatic flame temperature one shot. If you even assume this particular scenario where the products are known to me, adiabatic flame temperature is calculated by balancing the enthalpies of the reactant and product mixtures. How to calculate this?

First of all, it is an iterative process. Now, what is the iteration here? I assume a temperature T, T_{ad}, T adiabatic. Enthalpy of reactant mixture is calculated because T_R is known, so H_R is known to me.

Now, I calculate H_P by assuming a temperature T_{ad}. That is n_i (h_{fi} + Δh), this is the absolute enthalpy, enthalpy of formation of each species plus its sensible enthalpy multiplied by the number of moles of the particular species then summed up for all the species that will be H_P.

Now, I do not know the temperature I have assumed the temperature. Please understand I am assuming a temperature for calculating this. Now, I have to check whether H_P, value what I got here is same as that of the reactants, that is I have to check if $H_P = H_R$. I check this. If it is yes then what I assumed is correct. If it is no then I have to assume another temperature.

Based upon the difference between the H_P and H_R, I will assume a different temperature and another value of T_P or product temperature or adiabatic temperature is guessed and again calculate H_P. So, another temperature is guessed and again calculate H_P.

Now, see whether this condition is satisfied or not, ok. So, it is a iterative process. Please understand there no straightforward way, iteratively we will have to do it. Even when there is an assumption of complete combustion where the constituents of the product mixture is known you do this.

Finally, I stop the calculation when H_P - H_R is very very low, say 10^{-5} or normalized value is less than 1 percent something like that.

So, this is the way you calculate the adiabatic flame temperature, but even after this iterative process what you get is much higher than what you measure. Because you assume this complete combustion which is not correct.

When the temperatures are more than say 2000 K which is easily seen in a combustion chamber the products of CO_2, H_2O does not remain and they dissociate into CO, H_2 and so on.

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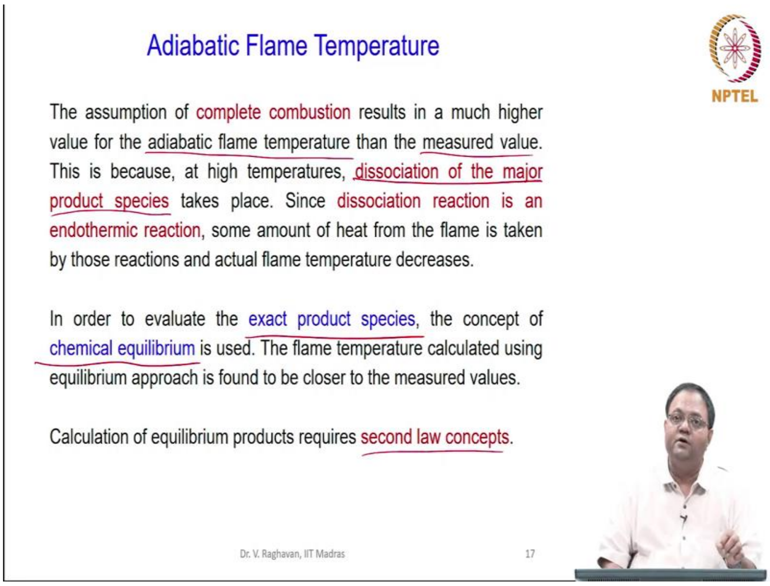

Adiabatic Flame Temperature

The assumption of complete combustion results in a much higher value for the adiabatic flame temperature than the measured value. This is because, at high temperatures, dissociation of the major product species takes place. Since dissociation reaction is an endothermic reaction, some amount of heat from the flame is taken by those reactions and actual flame temperature decreases.

In order to evaluate the exact product species, the concept of chemical equilibrium is used. The flame temperature calculated using equilibrium approach is found to be closer to the measured values.

Calculation of equilibrium products requires second law concepts.

So, the assumption of complete combustion results in a higher value, much higher value of adiabatic flame temperature than the measured value because the dissociation of major products occurs and this dissociation reaction is an endothermic reaction.

So, when you want to split CO_2 you have to supply energy. That energy is taken from the combustion chamber itself, so that CO_2 splits into CO and 1/2 O_2 taking energy from the combustion chamber and lowering its temperature.

The actual temperature is lesser than the calculated value without assuming any dissociation. When you assume no dissociation, you end up in calculating higher temperatures, over predicting the temperatures.

Now, how will you do the exact calculation then? Is there any way or not? Yes. So, first of all we have to get exact product species which is going to contribute to the product mixture. How we are going to do that? We will invoke what is called chemical equilibrium for that.

Chemical equilibrium is going to be the next topic what we are going to see which involves second law concepts, by using this we will see what is the amount of product which are there.

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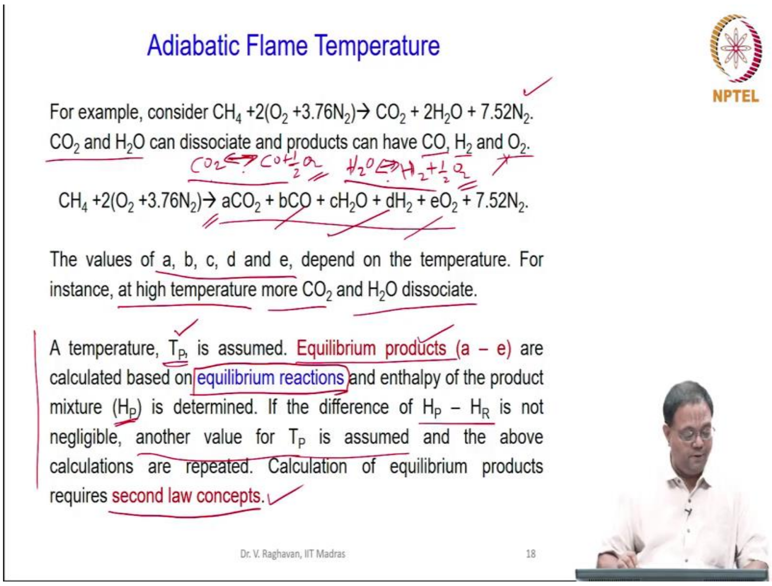

Adiabatic Flame Temperature

For example, consider $CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2$. CO_2 and H_2O can dissociate and products can have CO, H_2 and O_2.

$CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$ $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$

$CH_4 + 2(O_2 + 3.76N_2) \rightarrow aCO_2 + bCO + cH_2O + dH_2 + eO_2 + 7.52N_2$.

The values of a, b, c, d and e, depend on the temperature. For instance, at high temperature more CO_2 and H_2O dissociate.

A temperature, T_P, is assumed. Equilibrium products (a – e) are calculated based on equilibrium reactions and enthalpy of the product mixture (H_P) is determined. If the difference of $H_P - H_R$ is not negligible, another value for T_P is assumed and the above calculations are repeated. Calculation of equilibrium products requires second law concepts.

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See for example, let us consider methane reaction. Complete stoichiometric reaction is given here

$$CH_4 + 2\,(O_2 + 3.76\,N_2) \rightarrow 1CO_2 + 2H_2O + 7.52\,N_2.$$

Now, major products CO_2 and H_2O can dissociate to form CO, H_2 and O_2. Why O_2 because CO_2 when it splits it will produce ½ O_2. Similarly, H_2O splits to produce ½ O_2, when this dissociation takes place O_2 is formed. That will also be there in the product.

$$CH_4 + 2\,(O_2 + 3.76\,N_2) \rightarrow aCO_2 + bCO + cH_2O + dH_2 + eO_2 + 7.52\,N_2.$$

So, in the product now you will have CO_2, CO, H_2O H_2 and O_2. I do not know the number of moles of this as I told you it is not easy. We have already seen before because you have a carbon hydrogen and O balance but you have 5 unknowns. So, you cannot get the values easily. Even we if we take a carbon balance a + b = 1. How will we solve for a + b? it is not easy to solve this. What we do here is we have to find equilibrium products, that is if we use what I have written here these equations there are two more equations I am forming here, which defines how the CO is formed from CO_2 and H_2, is formed H_2O. So, what you have is CO, H_2 and O_2 these 3 are present in this. From the major species CO_2, how CO and O_2 are formed that is defined by this reaction? Similarly, from H_2O how H_2 and O_2 are formed is defined by this reaction.

$$CO_2 \Longleftrightarrow CO + \frac{1}{2} O_2$$

$$H_2O \Longleftrightarrow H_2 + \frac{1}{2} O_2$$

So, if you somehow couple these two reactions. Already, we have 3 equations from atom balances C, H and O. If you somehow take these two equations into account and form two more equations, there will be 5 equations and 5 unknowns which can be solved to get the values of a, b, c, d and e. These two equations will not perform in a unique way always, they are highly dependent on temperature.

If temperature is higher, more CO_2 will dissociate, more H_2O will dissociate, if temperature is lower than you will not see so much formation of CO. For instance, at high temperature more CO_2 and H_2O will dissociate. That is the important thing here.

So, I am trying to link two more equations to this equation to form 5 equations to find the 5 unknowns. Now, while doing so, there are some concepts which you have to invoke. We will see later.

Now, here how will you calculate the temperature? First you again assume temperature, when you know the product or we do not know the product, first step is to assume temperature because these values are dependent on temperature.

So, I assume a temperature T_P, then I calculate the equilibrium products. The equilibrium products will give you how to determine the values of a, b, c, d, and e for which I am going to invoke 3 atom balance equations for C, H, and O and two more equations from these two reactions.

I try to get the composition a, b, c, d and e for the particular temperature T_P, because these values are dependent only on particular temperature. For these two equations the extent at which the dissociation take place will depend on the temperature. So, I take the help of chemical equilibrium to calculate this.

So, these two equations what I have written here CO_2 giving CO + ½ O_2, H_2O giving H_2 + ½ O_2, they are called equilibrium reactions. So, with the help of equilibrium reactions I am trying to get the equilibrium product composition and for a given temperature T_P.

Now, once I know the composition, I calculate H_P. There is no problem in calculating H_P once I know the composition. Since, a, b, c, d and e are known I can substitute here and calculate the absolute energy of these species use the chain rule to get the H_P value.

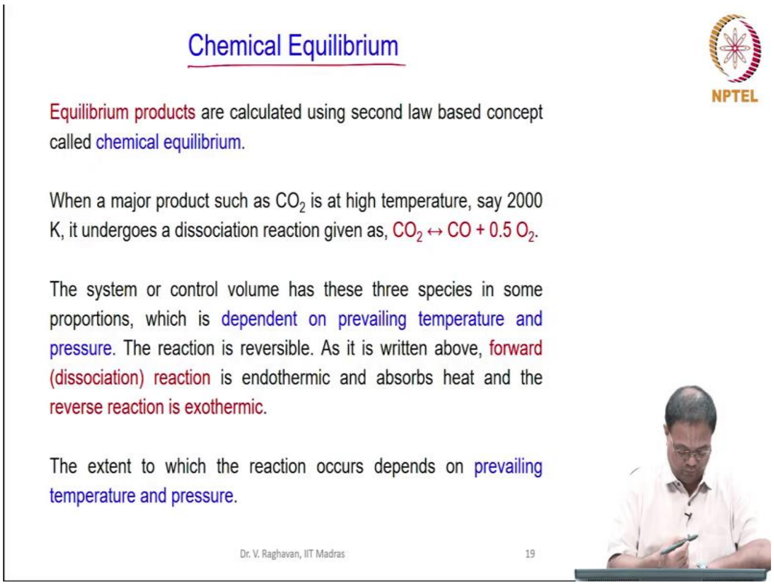
Now, comes the problem, I check this H_P - H_R, they are not same or they are not negligibly small. So, what will I do? Then, I have to reassume the value of temperature again and with this value, I have to again calculate the equilibrium product using these two equations plus 3 atom balance, calculate the H_P and then check. So, this is an iterative process.

Additional step is to calculate the equilibrium product using the equilibrium reactions, using a concept called chemical equilibrium which depends on second law.

So, our temperature calculation is not just first law alone, we have to use the concept related to second law also to get the equilibrium, product composition and for which you need a set of equations called equilibrium equations which are actually elementary equations in nature.

Actually, I have to put an arrow like this two-sided arrow, I have to put indicating that this reaction unlike other reaction which will take place in the forward direction, can take place in the reverse direction also. So, CO_2 giving CO + ½ O_2, at the same time I can also see that CO + ½ O_2 will also give CO_2.

So, based on what condition which side is favoured, or in other words, based upon temperature and pressure how much CO_2 is left how much CO is formed, how much O_2 is formed etcetera, can be determined. For that you need second law concepts. (Refer Slide Time: 26:51)



Chemical Equilibrium

Equilibrium products are calculated using second law based concept called chemical equilibrium.

When a major product such as CO_2 is at high temperature, say 2000 K, it undergoes a dissociation reaction given as, $CO_2 \leftrightarrow CO + 0.5\ O_2$.

The system or control volume has these three species in some proportions, which is dependent on prevailing temperature and pressure. The reaction is reversible. As it is written above, forward (dissociation) reaction is endothermic and absorbs heat and the reverse reaction is exothermic.

The extent to which the reaction occurs depends on prevailing temperature and pressure.

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So, that is what the second law concept. To invoke that we do what is called the chemical equilibrium.