Fundamentals of Combustion

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Lecture – 06

Stoichiometry– Part 1

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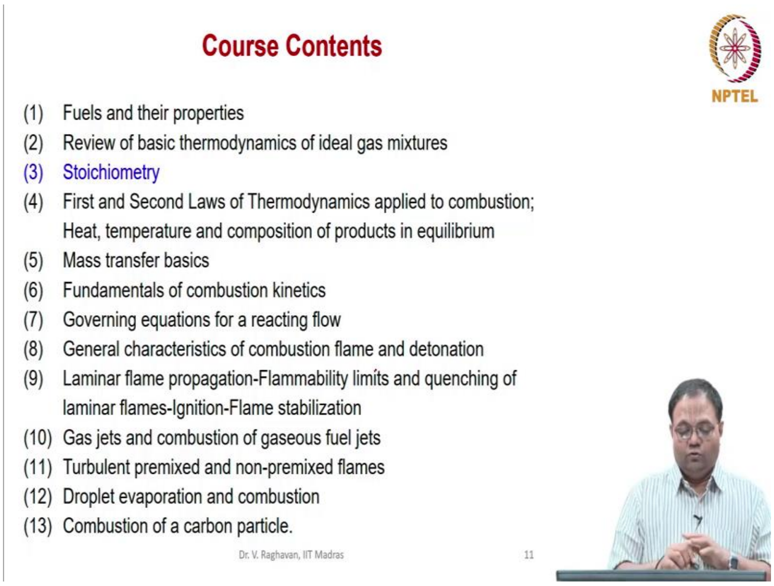

So, this finishes the review of thermodynamics for ideal gas mixtures. The next topic is Stoichiometry.

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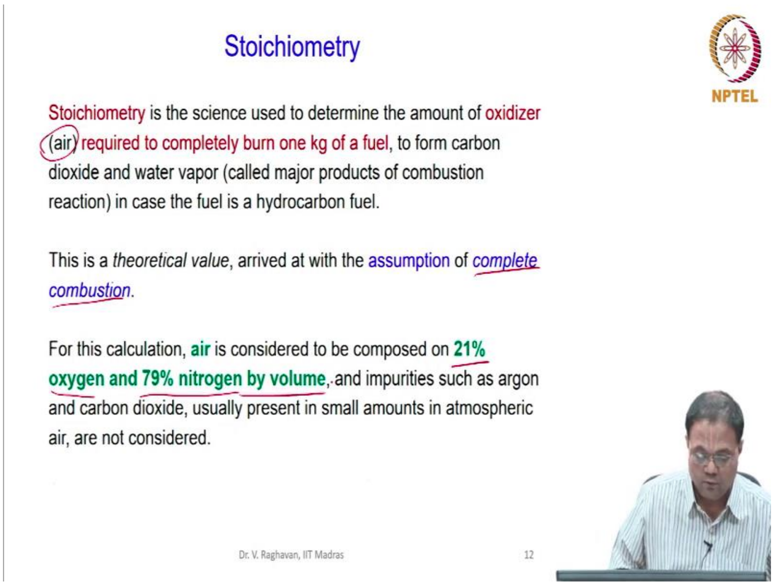

Stoichiometry is the science which deals with calculation of the amount of oxidizer required to burn a given quantity of fuel. We have discussed in beginning that when you want to know say you are designing a burner. The burner has a given power rating.

It has to generate so much power, say 2 kilo Watt, 5 kilo Watt etcetera. Then based upon the calorific value of the fuel you know what is the amount of fuel, that has to be supplied here ok. That mass flow rate of the fuel is determined by the power rating of the burner.

So, I need say x kgs per second of fuel to be supplied to the burner. But to oxidise this fuel what is the mass of oxygen required or oxidizer required? So, always you cannot use oxygen.

Normally we use air as the oxidizer, air has 21 percent of oxygen and 79 percent of nitrogen by volume. So, you have to use this. So, how will you calculate the amount of air required for burning the given amount of fuel?

In a flow combustion, that is you are supplying continuously some amount of fuel and it has to be burnt. So, you have to continue supply the given amount of oxidizer also in order to burn this. How to calculate this value? That is dealt by stoichiometry.

Now, stoichiometry is only a theoretical calculation. What we first assume here is, the fuel completely burns. This again you have to recall that we are only considering major products of combustion, that is CO_2 and H_2O; when a hydrocarbon fuel is burnt.

Hydrocarbon fuel all the carbon in it is converted into CO_2 and hydrogen is converted into H_2O. Only CO_2 and H_2O are formed and fuel is not left; so, that is what we are considering.

Similarly, all the oxygen should be consumed. We are trying to calculate only the enough amount of oxygen required for the combustion; that means, all the oxygen should be consumed. So, this is a theoretical calculation which will give you the amount of oxygen required. But, in practice you can supply whatever amount you want maybe we will supply excess, to ensure that all the fuel is consumed.

So, the complete combustion is assumed here; that is the important thing. Now, when I say air, I take only standard atmospheric air, but atmospheric air has lot of impurities.

But standard air I am considering; standard air is nothing but it has 21 percent of oxygen and 79 percent of nitrogen by volume; that is the standard air I take. The other impurities like argon, carbon dioxide etcetera which are usually present in the atmospheric air is not taken into consideration here.

That means, if we say air it will contain 21% of oxygen and 79% of nitrogen by volume. You have to remember its by volume, ok.

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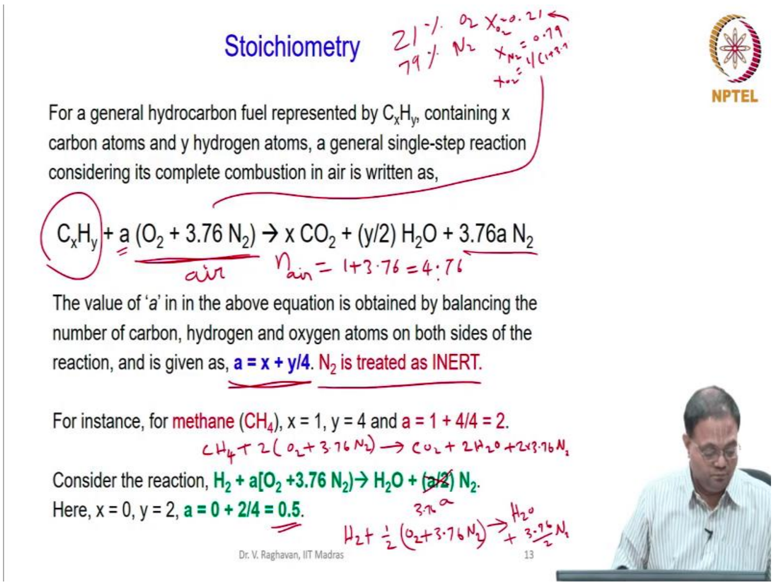

Now, let us go and do this calculation; before coming to hydrocarbon, I want to indicate that how will you calculate air, how will you write the number of moles of air? So, you can see this, this represents the air.

$$O_2 + 3.76\ N_2$$

When I say mole fractions of air; air has 21% by volume of O_2, 79% by volume of N_2. Its volume fraction is known that is nothing, but the mole fraction.

Mole fraction of oxygen is 0.21. I will say x O_2 is 0.21, similarly x N_2 is 0.79. These are mole fractions of the air what we consider. So, now whether this makes sense, this is 1 mole of oxygen I am saying; 1 mole of oxygen.

If 1 mole of oxygen should be present in the air what I take for combustion, how much moles of N_2 should be present? That is 3.76; how it comes? 79/21; so, 0.79/0.21; so, that would be this.

If I want 1 mole of oxygen, here everything is written in mole terms, kilomoles. If I want 1 kilomole of oxygen, then when I supply air for this 3.76 kilomoles of nitrogen also will enter the combustion chamber.

This is what you would understand here; so, that the mole fractions will be calculated. Here from this you can calculate the mole fraction like this. So, here what is this? So, x O_2 will be equal to 1/(1+3.76) which will be equal to 0.21 and so on. So, we have to re calculate and see. This is the equation I write.

$$C_xH_y + a\,(O_2 + 3.76\,N_2) \rightarrow x\,CO_2 + (y/2)\,H_2O + 3.76a\,N_2$$

So, this is air, this represents air and this is any hydrocarbon; if I put x = 1, y = 4 its methane. So, x general hydrocarbon C_xH_y, x carbon atoms and y hydrogen atoms are present in this and I do not know how much air to be supplied.

So, I put ‘a’ here; ‘a’ kilomoles of air. I always take 1 kilomole of fuel. So, here I do not want to put 1 here. 1 kilomole of fuel I take and for combusting it completely I have to supply ‘a’ kilomoles of oxygen ok. Since I supply air I have to also supply 3.76 kilomoles of nitrogen and I get the products. I assume complete combustion, two assumptions are made here.

The first assumption is complete combustion, where all the x C atoms are converted into CO_2 molecules. So, xCO_2; that means, you say carbon balance left hand side number of carbon atoms is x, right hand side also C_x you can see in the front. So, x atoms are there. Now, y is the number of hydrogen atoms, now here $(y/2)\times H_2$; that means, y H atoms are present.

I do only the atom balances to get this. Now, what will you do with nitrogen? Nitrogen I assume as inert, this is the second assumption what I make ok. Nitrogen is assumed as inert and it is good for all practical purposes. No harm in it even if nitrogen reacts with oxygen to form some nitric oxide, they are very very minimum like negligible in this; but even negligible amount is also not good for us.

So, even if it reacts, we need not worry about those numbers here for at least calculation of the required amount of air; so, I treat nitrogen as inert. So, you can see that 3.76 times ‘a’ kilomoles of nitrogen just appears in the product like this without having any reaction; so, it is inert. Just it comes in the product.

So, nitrogen is automatically balanced. What is the number of moles of nitrogen in the left hand side? 3.76 times ‘a’ and in right hand side it is 3.76 times ‘a’. So, now, when you do O balance you will get the value of ‘a’ as x + y/4, that is it. So; that means, when we want to completely burn an hydrocarbon with x C atoms and y H atoms, then you need number of moles of oxygen equal to x + y/4.

For methane x = 1, y = 4 then ‘a’ = 2. So, I can write the equation for methane as,

$$CH_4 + 2(O_2 + 3.76\,N_2) \rightarrow 1CO_2 + 2H_2O + 2\times3.76\,N_2$$

CH_4 1 mole of methane plus 2 moles of air, that is air means O_2 is only 1 mole and nitrogen is this. Having 1 carbon atom; so, $1CO_2$ plus 4 hydrogen; so, $2H_2O$. $2H_2O$ + 2×3.76 times N_2. No oxygen will be there it is fully consumed.

Complete combustion oxygen is fully consumed because, you are only trying to find the exact quantity of oxygen required. For hydrogen; so, I do not have C, hydrogen you take H_2 and I am combusting hydrogen with the air. So, a(O_2 + 3.76 N_2) giving H_2O plus actually it should be a/2, (a/2)O_2; because now you need only this. You can also write like this. So, 'a' into N_2 ok. Now we can see x equal to 0 here y = 2; so, a = 0.5 ok. So, here 0.5 times sorry 3.76 times 'a' into N_2 that is what you have to write here, 3.76 times into 'a' into N_2. Now 'a' is 0.5 so, substitute 'a'. So, this was a mistake here. So, H_2 plus 'a' times O_2 plus 3.76 N_2 give H_2O plus 3.76 times 'a' times N_2.

So, now you can find this is half. So, we can write the equation as H_2 plus half O_2 plus 3.76 times N_2 giving H_2O plus 3.76 by 2 times N_2 ok. So, this is the equation you get, hydrogen combustion with air.

$$H_2 + a(O_2 + 3.76\ N_2) \rightarrow H_2O + 3.76a\ N_2.$$

Now, you determine the number of moles of air required for burning. When I say number of moles of air, see when I say number of moles of oxygen it is 1 whereas, number of moles of nitrogen it is 3.76. So, the number of moles of air is 1 plus 3.76.

So, 1, just add the number of moles of oxygen and nitrogen in this. Number of moles of air is written as 1 + 3.76 = 4.76, same $n = n_1 + n_2$. There are two components: one is oxygen, another one is nitrogen; so, add them. So, n air is 4.76. So, if you want to supply 1 kilomole of oxygen, you have to supply 4.76 kilomoles of air.

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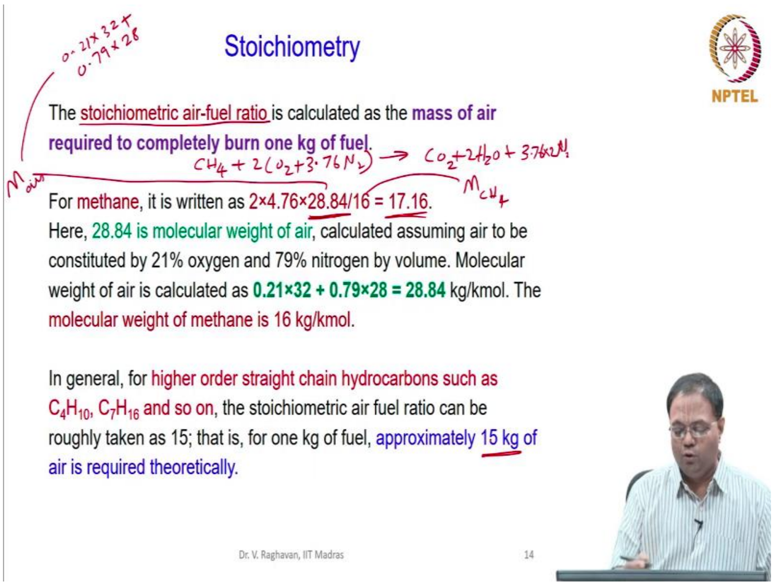

Now, another definition is stoichiometric air fuel ratio is nothing, but the mass of the air required to completely burn one kg of fuel. Now, we have found what? The number of moles required to burn 1 mole of fuel.

Here, in this previous slide 1 mole of fuel requires a moles of oxidizer, air. That is what we have found here is molar basis. Now, we are trying to do ratios in mass basis, stoichiometric air fuel ratio is mass of air required to burn one kg of fuel ok.

Now, for methane I will write the equation,

$$CH_4 + 2(O_2 + 3.76\ N_2) \rightarrow 1CO_2 + 2H_2O + 2\times3.76\ N_2$$

So, this is the equation $CH_4 + 2(O_2 + 3.76\ N_2)$ gives $CO_2 + 2H_2O$ plus 2×3.76 into N_2. So, this is the equation. Now, reactant side we will see 2 into 4.76, total number of moles in air into, this is the molecule weight of air ok; divided by molecular weight of methane. So, this is molecular weight of methane and this is molecular weight of air ok. How we get this molecular weight of air? $0.21\times32 + 0.79\times28$, where 32 is the molecular weight of oxygen and 28 is the molecular weight of nitrogen and mole fraction of oxygen is 0.21. So, 0.21 times 32 plus 0.79 times 28, that will be the molecular weight of air.

And, that is 28.84 ok, molecular weight of methane is 16. So, number of moles of the air is 2 times the number of moles of this each component, add that together. So, 2 times 4.76 times 2 times 4.76 is the number of moles of air into its molecular weight is 28.84 ok, that is the mass of the air divided by 1 mole of methane into its molecular weight is 16. So, this is the ratio.

So; that means, if you want burn 1 kilogram of methane, you should supply 17.16 kilograms of air; theoretically to burn it completely.

So, I have given here 28.84 is the molecular weight of air it is calculated like this and the molecular weight of methane is this. Now, when you take higher hydrocarbons, straight chain for example, C_4H_{10} is butane, then heptane and so on.

What happens is this is very high; methane 17, but it actually decreases and becomes almost a constant. So, you can say that for higher hydrocarbons straight chain hydrocarbons, you will get stoichiometric air fuel ratio as around 15. That means, you need roughly 15 kgs of air to burn one kg of hydrocarbon fuel; you can try to do a calculation and see.

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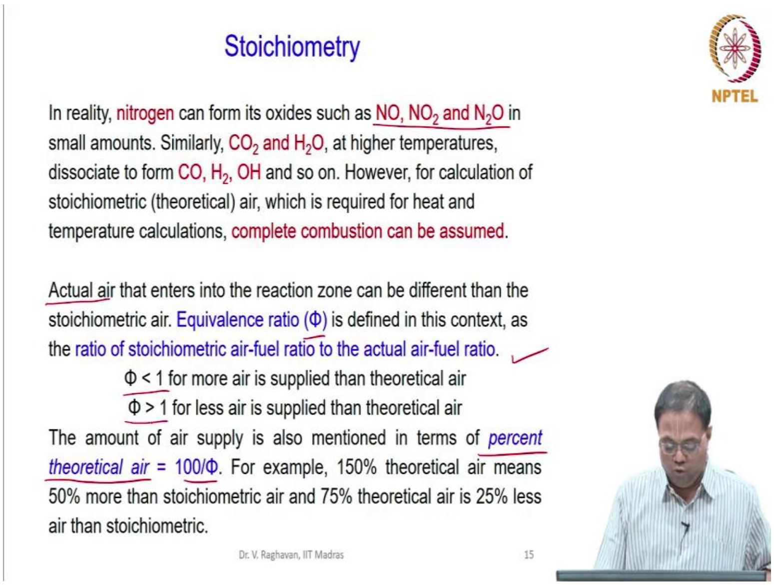

Now, I told you we have assumed that nitrogen is inert. But, as I told you in reality where the temperatures are high enough and availability of oxygen is also more, then what happens is the nitric oxides can be formed; NO, NO_2, N_2O etcetera they can form. But they are not very high in amount; when compared to CO_2 and H_2O, they will be not very high.

One more thing what can happen is the temperatures when they exceed say 2000 Kelvin, CO_2 will not remain as CO_2; it will break into CO and O_2. This is called dissociation, so that also can happen. Similarly, still higher temperature than say 2000 it may be say, 2500 or something; you will see that water vapour also can dissociate to form H_2 and some radicals like OH can form.

This means that the products need not be just CO_2 and H_2O, it can also have all other things. But, please understand that theoretical calculation to calculate the required number of oxygen to burn a given amount of fuel, we do stoichiometry. So, there is nothing wrong in assuming this. Only two major products are formed; complete combustion is there.

But, in actual scenario we will not only use the theoretical air, we will either do combustion with excess air or we will do staged combustion. There are multiple stages in the combustion. In one stage we will only supply 80 percent of the required air, theoretically calculated air; what do we call stoichiometric air 80 percent.

In another stage we will supply say remaining 20 percent and in the later stage we can also supply excess air. So, that the total air supplied will be more than the stoichiometric air. That is also possible. The actual air that enters the reaction zone or the combustion chamber can be different than and it is actually different in several applications, than the stoichiometric air.

So, based upon this we define what is called an equivalence ratio phi, here equivalence ratio is nothing but the ratio of stoichiometric air fuel ratio; what we calculate by assuming complete combustion, to the actual air fuel ratio which is supplied to the combustion chamber. So, phi is equal to stoichiometric air fuel ratio divided by the actual air fuel ratio ok.

Stoichiometric air fuel ratio is the mass of air divided by the mass of the fuel under theoretical conditions, stoichiometric conditions. Actual air fuel ratio is the mass of the air actually supplied to the combustion chamber divided by the mass of the fuel.

Now, if they are equal phi = 1; that means, that you are only supplying the stoichiometric air. If phi < 1, phi is less than 1 then you are supplying the air which is more than the stoichiometric air.

That means, if we mix fuel and air such that you have more air than required or calculated by stoichiometric equations, then that is called fuel lean mixture. Because, fuel is less than what it should be for the stoichiometric mixture. Similarly, if phi > 1, phi is greater than 1 then you will have rich fuel less air.

So, this is very important term, equivalence ratio is a very important quantity. That is what is going to be specified. For any combustion number we will specify the air supply by using equivalence ratio or you can use we can say percent theoretical air which is also dependent on equivalence ratio.

So, this is very important. Once you decide the amount of air theoretically to be supplied, then in actual process we can alter that. We can also do staged combustion as I told you and in one of the stage phi may be greater than 1, in another stage phi may be less than 1 and so on. So, total overall the phi may be less than 1, but in stages we can have our own controls.

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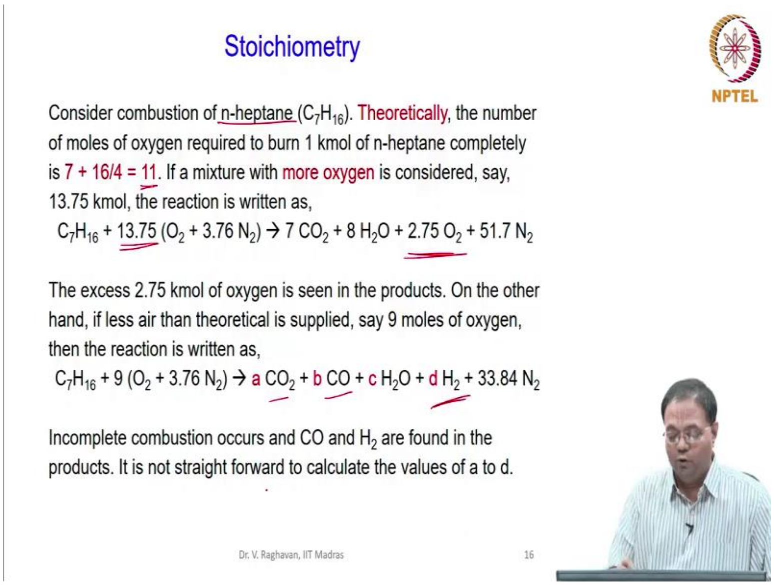

Now, let us consider n-heptane as a fuel C_7H_{16}. Theoretically, the number of moles of oxygen required to burn 1 kilomole of heptane completely is x + y/4, where x = 7 here and y = 16. So, you will need number of moles of oxygen to be 11. So, you can write the equation, Say now let us consider more oxygen supplied.

$$C_7H_{16} + 13.75\ (O_2 + 3.76\ N_2) \rightarrow 7\ CO_2 + 8\ H_2O + 2.75\ O_2 + 51.7\ N_2$$

So that means, you only want 11 kilomole per kilomole of fuel; I supply 13.75 kilomoles instead of 11 kilomoles of oxygen. So, I supply this; now if I complete the equation you can see that when I assume complete combustion which is actually possible here, then you see that I get O_2 in the products.

So, the rest 13.75 minus 11, the 2.75 appears in the product, excess 2.75 kilomole of oxygen is seen in the products. On the other hand, if less air is supplied, say 9 moles of oxygen, 9 moles or kilomoles, then it is not easy to write the equation.

So, here when you supply more air it is very easy to write the equation, because oxygen is considered inert; again it does not have much fuel to react with. So, it just appears as oxygen in the products.

On the other hand, now what I do is I now consider only less amount of this oxygen,

$$C_7H_{16} + 9\ (O_2 + 3.76\ N_2) \rightarrow a\ CO_2 + b\ CO + c\ H_2O + d\ H_2 + 33.84\ N_2$$

I am not supplying 11 kilomoles I am supplying only 9 kilomoles here. So, you see I do not know what will happen. Let us assume this. All the carbon is not going to be converted into CO_2; obviously, because you do not have enough oxygen.

So, some of the carbon is converted to CO_2, but some will be converted only to CO because efficiency. Similarly, some of the hydrogen may not burn, we do not know what is true or false; because this a, b, c, d which I put in the right hand side is not just atom balances here. We have to incur other relationships for calculating a, b, c, d here.

But one thumb rule is hydrogen normally is much highly reactive species than carbon. So, what happens is hydrogen will first try to take all the possible oxygen. So, conversion of hydrogen into water vapour will first occur. Then within the available oxygen the number of moles of CO or CO_2 will be decided upon.

But, if you starve the mixture with more and more fuel and lesser and lesser oxygen; then you can see hydrogen appearing in the products. So, but it is not easy to complete this reaction. So, incomplete combustion occurs CO and H_2 form. But it is not straightforward for us to calculate the values of a, b, c, d in the right hand side of this.

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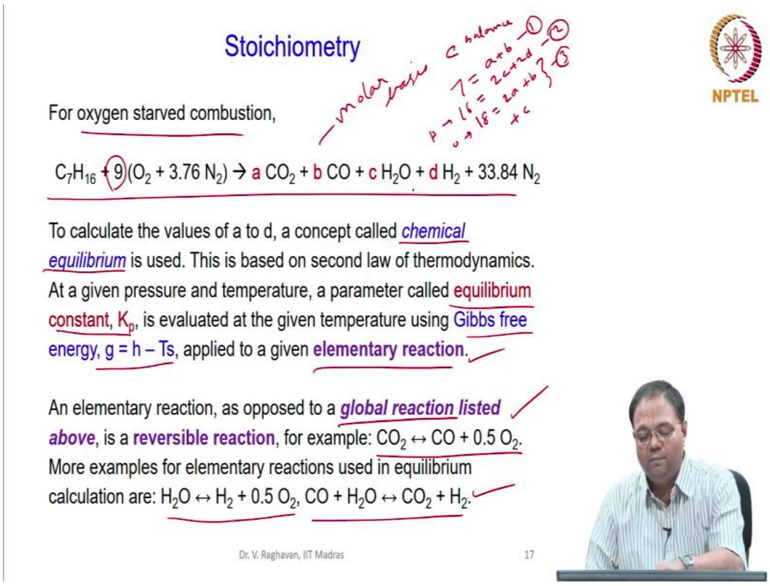

Again I am taking the same equation for oxygen starved combustion, you see that we have to use what is called as concept of chemical equilibrium; which is dependent on the second law of thermodynamics. What I am saying is we do not have sufficient data to analyze this.

We need temperature, pressure at which these products are going to be present. And, based upon that we have to calculate what is called an equilibrium constant K_p and for that we need some free energy calculations Gibbs free energy, $g = h - Ts$. So, enthalpy, entropy will be the; whenever I say entropy then second law is involved in this.

A second law based property is entropy and based upon that a derived property is g, Gibbs free energy. So, $g = h – Ts$, that will be used. This equation basically is the mechanism of what are the reactants and what are the products. But this equation is not going to occur like this when the fuel is oxidized into products.

So, we need lot of elementary equations. These are the other things which we need to study before addressing the problem of oxygen starved combustion. That is what we should understand. This equation what I have listed here, basically if you write say instead of 9 you write 11, that is the stoichiometric equation; that is the representation of the overall global reaction.

So, I say global reaction, but this global reaction, please understand it is written in molar basis. On the other hand, when I say elementary reaction, I will write in molecular basis. The examples of elementary reactions are this $H_2O \rightarrow H_2 + (1/2)\ O_2$.

Similarly, $CO + H_2O \rightarrow CO_2 + H_2$. These are all elementary reaction written in molecular basis. I will explain this more when we see the combustion kinetics.

But we need information now to calculate a, b, c, d you need to know the temperature or pressure at which the products are; these are products they are going to be there, at what temperature and pressure. Then we need to calculate equilibrium constant, constant K_p based upon the temperature which depends on the Gibbs free energy.

Then we need to use these K_p values on elementary reactions like these and CO_2. So, basically you have to use this; see for example, very easily you can understand that C balance can be done. There are four unknowns here a, b, c, d. Now, N is already balanced. So, you have three components C, H, O; it will give three equations. Say carbon balance left hand side is 7, right hand side a + b.

So, I can write carbon balance as 7 = a + b. This is equation 1, then second is H balance 16 = 2c + 2d; this is equation 2. Then O balance, this is H balance and this is O balance I will say; O balance gives here 18 left hand side O atoms, its 2a + b + c ok. So, this is the 3rd equation I have, but four unknowns are there.

So, that is what I said that it is not possible for us to solve this. So, we have to take one of these equations here and do the equilibrium calculation in order to find the fourth product. This may not be due to oxygen starved combustion.

Still, we can have 11 here instead of 9 we can have 11, but CO_2 can dissociate to form CO and O_2 ok. Similarly, H_2O can dissociate to form H_2 and O_2 and so on. In such cases also, the number of unknowns in the right hand side will increase and we have to invoke the chemical equilibrium approach.

So, we will see that in later, but I want to just let you know this. When you do your fuel lean combustion, excess oxygen, then it is easy to write the equations like this; assuming again the complete combustion which is possible here. When there is an oxygen starved combustion, we need to use chemical equilibrium to close the loop.

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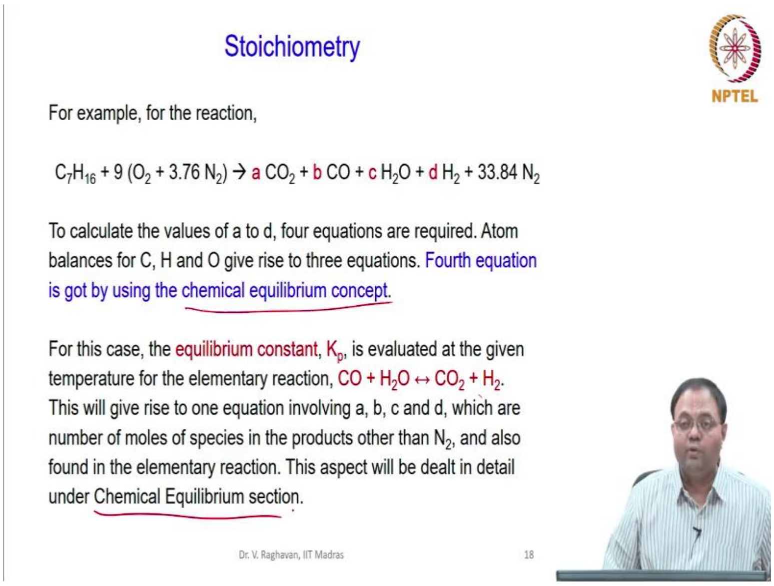

That is what I have explained here, to calculate the values of a to d, four equations are required. Atom balance C, H, O gives three equations and the fourth equation is got by chemical equilibrium. Now, for this particular case we can use this equation. I have shown three elementary equations in the in this slide; $CO_2 \rightarrow CO + (1/2) O_2$, $H_2O \rightarrow H_2 + (1/2) O_2$.

But you need only one more equation to solve for which you have to find the K_p value and plug it. What equation you will choose?

Let us choose this because, this has all the species involved in this CO_2, CO, H_2O and H_2. So, CO_2, CO, H_2O and H_2 all these four species are there in this. So, if you use this equation, then we can have one more equation which has a, b, c, d in it.

How will you do it? We will explain later. Normally what we do is we will invoke this equation elementary equation; this is called water gas shift reaction. This I will explain again in more detail later. This equation you invoke, find K_p of that, write an equation in terms of a, b, c, d. But, unlike these atom balance equations which are linear equations when you use K_p, for this you get a non-linear equation.

If one of the equations in the set is non-linear, then you have to solve a set of non-linear equations to find the values of a, b and c, d. In this way calculating the products are not so straightforward. This will be dealt in chemical equilibrium section later.