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Lecture - 31

Good morning. So, yesterday we finished our discussion on the nozzles and then I said in the last class that we are going to take up the combustion next. So, first of all why do we need to talk about combustion, we have been discussing chemical rockets and the source of energy for propulsion is created by chemical reaction in chemical rockets. Therefore, we have seen that the parameters that are important as far as the rocket performance is concerned are P c naught T c naught and gamma.

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All the performance indices are functions of this parameters. P c naught is the pressure, which we have seen that the higher the pressure is the better it is, but there is a limitation. So, that is that dictated by the supply. T c naught; however is the combustion chamber temperature again the higher the value T c naught is the higher thrust will be generated.

So, in order to analyze the flows to the rocket as well as to estimate the thrust etcetera we need to know the temperature. And gamma is the ratio of specific heats C p by C v, which is essentially a function of composition. That is the composition of the burn product after the reactions. Therefore, in order to complete analyze the problem apart

from P c naught, we need to know this two also T c naught and gamma, other words I can say that we need to know the final temperature of the propellants of the after reaction as well as the composition. So, now, we are going to focus on these two aspects. So, let us say that we have two propellants A and B with sudden amount the small a and b coming into the combustion chamber and after the reaction we get something like this etcetera.

So, we have various products after the reaction we get this product. Now, the composition means that we need to know this, what is the final distribution of the product that is what the products we need to know and at how much of this products are present in the reactant mixture also we need to know and therefore, we need to analyze the chemistry of the process. So, to do that first of all, we have to see whether this side that what products will be there and how much will be there is it arbitrary are there are some laws governing it. This depends on conservation of atomic spaces. So, far we have talk about three conservation laws that is conservation of mass, momentum and energy. These were all global parameters and based on this conservation laws we derived all the equations for the performance of the rocket etcetera.

Now, when we come to the chemistry rather the composition then once more thing that one more conservation law is applicable which is conservation of atomic spaces? We have seen the conservation of mass; we say that the mass coming into the control volume is equal to the mark living the control volume as long as there is no accumulation of mass. But the number of atoms of an atom mix species must also be conserved in a particularly in a chemical reaction, but we mean by that, this molecule A and molecule B are made of some atoms right. When the reaction happens in the product side the total number of each atom must also be conserved. So, if consider a generalize chemical reaction, let us say, this is the generalize chemical reaction, actually series of reactions so many reactions in this and reactions in total.

Here this side represents the reactants, this side represents the products. So, left hand side is reactants and right hand side is product. Now, according to the conservation of atomic species, once this reactant side is specified the number of moles of the reactants, which essentially this things mu I dash are specified the values of mu I double dash that is the composition of the product side is also constraint it is not arbitrary. And this constraint is due to the conservation of atomic species, so for each species A, as we have mentioned here.

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We define, let us say for each species A, we define small a, as the number of that particular species present in a particular molecular species m i. So, m i is my molecular species. This consist of varies atomic species. So, I can write m i as made up of various atomic species say A 1 a 1, A 2 small a 2 then A 3 small a 3 etcetera.

Here A 1, A 2, A 3 represents my atomic species for example, it can be hydrogen, it can be oxygen, it can be carbon etcetera. And this small a 1, small a 2, small a 3 represent the number of atoms of this species present in that molecule. Let us look at an example, if I consider my at molecule to be water vapor H 2 O then m here is H 2 O, it can be written as H 2 O 1. So, here my A 1 is H, small a 1 is 2, A 2 is O, small a 2 is 1. That is the representation of my atomic species. Another example let us look at, ammonium per chloride N H 4 C 1 O 4, this typically a propellant, solid propellant. So, this can be written N 1 H 4 C 1 1 O 4 therefore, for this my A 1 is nitrogen, small a 1 is 1, A 2 is hydrogen, small a 2 is 4, A 3 is chorine, small a 3 is 1 and A 4 is oxygen, small a 4 is 4. So, this is the representation of a molecular species in terms of the atomic spaces.

Now, if I consider this form then if I go back to this equation now, the chemical reaction then I can write this chemical reaction as sigma i equal to 1 to N mu i dash A m i, I will represent by the atoms, atomic composition. Then this will become equal to. Now, this is not going to change. So, the overall this is also i, so for each molecule i, I can write it in terms of its atom. So, now, what happens is that during the chemical reaction the atomic species does not get consumed it just changes the composition changes that is one atom will move from say molecule to other molecule it does not vanish from the reaction. Similarly nothing new can arise also getting added. So, the atomic species maintain their identity only thing is that nor they may go into different molecule.

And that is why the atomic species is said to be conserved. So, the total number of any atomic species present in a reaction is conserved, if that is the case, if I look at let us say one of them, let us say A 1. Then how many atoms of A 1 are present, according to this, this term right. So, I can write this as sigma i equal to 1 to N mu i dash a 1 i this is in one of the species similarly form species there will be different molecules in which A 1 is present. This is equal to sigma i equal to 1 to N mu i double prime a 1 i and this is going to be a constant. So, this is the conservation of atomic species one, similarly for every species, atomic species A 1. Similarly for every atomic species we can get the conservation equation and as we can see that this is a algebraic equation.

This side the, this term is known, because we know what are the reactants coming in either fuel or oxidizer this term is known, this is the unknown, which we need to estimate. So, we have to notice one thing that, if we have N atomic species in a combustion system then for each species we can create one of these equations.

So therefore, there can be N algebraic equations can be constructed for this N atomic species. And then we can solve this for the composition; however, the problem is that there may be greater or less than N molecular species. For example, here as you can see there are four atomic species, but there is only one molecule species right. So therefore, that put some restriction into the solution passed we will not have enough number of equations. So, we have to get some additional equations which we will discuss later.

So, just to give an example lets us consider this reaction, hydrogen and chlorine reacting giving hydrogen collide right. So, this reaction can be written as one mole of hydrogen reacting with one mole of chlorine and 0 mole of H C l giving us 0 mole of hydrogen 0 mole of chlorine and two mole of hydrogen chloride. So, if I look at the atomic species H hydrogen. So, in the left hand side of this I have 1 into 2 plus 1 into 0 plus 1 into 0 that is 2 moles of hydrogen. And in the right hand side, this L H S, in the right hand side where

we have the hydrogen collide on the, we have 0 into 2 plus 0 into 0 plus 2 into 1 that is 2 in R H S. So, in the right hand also we have two hydrogen atoms. So, as we can see that this is balanced.

Hydrogen is essentially the number of hydrogen atoms are conserved. Similarly we can get first C l similarly for H C l so this is a balanced equation. Now, in reality here I have started with 2, but 2 may not be known, what will be known to us is that we have one mole of hydrogen one mole of C l how many moles of H c l will be produced. So, we do it like this. Then we find out there will be two moles of H C l that will be needed to balance this reaction. So, this is one set of equations that we will get. Now keep this in mind let us move little away and now define some of the parameters which are useful for combustion analysis. If I look at this equation or if I look at this equation I have a and b two molecules, one can be fuel other can be oxidizer.

Now, what is going to be the final equation as I said depression what is initially present right. It depends on small a and small b. So, we can represent it as the ratio of this two. Now, initial state can be represented as the ratio of this two amount of propellants right, amount of fuel and amount of oxidizer. So, there are various definitions, which are used for this. So, I will first define those things and later on we can use either one of those for our future analysis. What we are interested is in the weight of the reactant.

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And the weight of reactant are generally specified by fractions and ratios. So, one of such fraction is called mass fraction is designated by y. So, for i x species now, we have many many species present for the i x species, the mass fraction of i x species y i is given as the mass of i x species in the reaction volume divided by total mass of all the species taken together, that is the definition of mass fraction. We can notice one thing that, if I add the mass fraction of all the species then this numerator also become sigma i equal to 1 to N mu i then y i is equal to 1.

So therefore, summation of mass fraction of all the species is equal to 1, where N is the different species in a given system, there are N species present in the system. Another are factor that is used is called mole fraction given by kappa. So, this defined as number of moles of a given species i in the reaction volume divided by total number of moles present in the system, where here n i is number of moles of species i. Once again if I add, subscript I, if I add the mole fraction of all the species then the numerator becomes sigma i equal to 1 to N mu i. So, this is equal to 1.

So, once again mole fraction also is equal to 1. Now, it is convenient many times to use Daltons law of partial pressure to represent this in terms of partial pressure particularly for gaseous reactions. And most of the gaseous reactions are gaseous, if we represent in terms of partial pressure it helps us later on we will see in getting the values of k P etcetera. So, that we can get some more equations, which are required to close the problem. So, then we will define also in terms of partial pressure and no mole fraction is a useful tool in defining the partial pressure. So, let me come to that.

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So, from Daltons law of partial pressure partial, pressure of species i given by P i times volume equal to mole number of, moles of species i times universal gas constant time temperature, where R is our universal gas constant is equal to 8.314 joules per k g Kelvin right, this is the universal value . So therefore, kilo joule per k g Kelvin, yeah. So, this is the Daltons law of partial pressure then sorry, this is the partial pressure defined as and the total pressure from Daltons law of partial pressure is given like this. Now, combining this two, I can write it as R T by V sigma i equal to 1 to N times n i therefore, partial special species i divided by total pressure the actual pressure of the system is equal to n i upon sigma i equal to 1 to N n i. So, this is by definition is my mole fraction. Therefore, partial pressure is equal to mole fraction of species i times the total pressure of the system. So, this is another way of representing the relative composition in terms of mole fraction of different species.

Now, the third way of defining is fuel oxidant ratio given by F by O. So, this is defined as the mass of fuel divided by the mass of oxidant. For example, let us say if you are looking at hydrogen and oxygen that is cryogenic propellant. So, therefore, for this reaction we have 2 H 2 O plus O 2 given 2 H 2 O, for this, what is my fuel oxidizer ratio, what is my fuel here, hydrogen is the fuel. So, mass of the hydrogen divided by oxidizer is oxygen, mass of oxygen. So much mass of hydrogen we have, we have two moles and the molar mass is for hydrogen is atom is one gram per mole. So, for 2, it is two gram

right. So, 2 into 2 into 1 divided by sorry, 2 into 2 divided by atomic mass, molar mass of our oxygen atom is 16. So, this is 2 into 16. So, this is equal to 1 by 8.

Therefore, the fuel oxidizer ratio is 1 by 8 for this case and this is the stoichiometric reaction right. So, the theoretical fuel oxidizer ratio should be 1 by 8, if you are having hydrogen and oxygen as the propellants. Now, another important ratio, which is very widely used in most of the combustion literature is called equivalence ratio and in this course, I will also be using equivalent ratio most widely.

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So, let we look at equivalence ratio given by phi. So, equivalence ratio is defined as actual fuel to a ratio divided by fuel to a ratio that is s t represents for a stoichiometric reaction a process. Now, what is the stoichiometric process? Stoichiometric process is the process in which all products are in their most stable form, first of all and in the products side we do not have any reactant present. So, we have only product no reactants. So, both the fuel and oxidizer is completely used up we have only product that is what a stoichiometric ratio is stoichiometric process is.

So, therefore, the equivalence ratio is defined as the actual fuel oxidizer ratio divided by the stoichiometric fuel oxidizer ratio. Let we look at a example to clear this up, let us look at combustion of methane in oxygen. So, this gives me C H 4 plus 2 O 2 giving me C O 2 plus 2 H 2 O. So, this is a stoichiometric process, why? Because here we do not have any reactant or product present and these are stable species both carbon dioxide as

well as water vapor as stable species. But if I look at different proportion of the oxidizer and fuel for example, if I consider this lets say, we reduce the amount of oxygen that is present then the reaction will be C O plus 2 H 2 O.

Now, once you might argue that this is also there is no reactant present, but the point is carbon mono oxide is not a very stable species; C O is not a very stable species. In fact, C O can still react, for example, I can have another reaction C O plus half O 2 giving C O 2. So, C O can still react to give for the stable species like carbon dioxide. So, therefore, in this case it is not a stoichiometric reaction. So now, what I can write it as instead of writing it like this, if I say that all my species are the product side are going to be stable in that case what happens. Let me just look at that.

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 $f_{14} + \frac{3}{2}O_2 \rightarrow aCO_2 + bH_2O + CCH_4$ $= \frac{F/O}{(F/O)_{SF}}, \quad 4 \neq = 1$ $= (F/O)_{SF}, \quad 0 < \phi < 1 \rightarrow Fuel lean.$ $L > aO \rightarrow Fuel nich.$

Once again I take C H 4 plus 3 by 2 O 2, I get C O 2 plus H 2 O right, 2 H 2 O. Now, here I have 1.5 times 2, that is three atoms of oxygen, here I have four atoms of oxygen that is not possible right. Only three atoms of oxygen will take part in a reaction. So, then what happens is that some of the methane will remain unburn. So, I will have a, b, c of methane. I am not going to have the full reaction burning all the methane some of the methane will remain unburn then this a, b and c is something that we need to estimate, let can be done very easily. So, a stoichiometric reaction is define as unique reaction in which all the reactants are consumed and the product species are stable. Therefore, this is the most economical reaction, if you look at it, you do not have an unburned fuel. So, all the energy has been released you do not have any unburned oxidizer. So, you are not essentially supply anything extra. So therefore, stoichiometric reaction is the most economical reaction. Now, coming back to the stoichiometric reaction then rather coming back to equivalence ratio then we define it like this.

Now, let us see, if phi is equal to 1. Then what type of reaction we have? We have stoichiometric reaction; this is known this is fixed. This is equal to this we has stoichiometric reaction. If phi is less than 1, it is in between 0 and 1 of course, it cannot be less than 0, phi is between 0 and 1 that is the actual fuel oxidizer ratio is less than the stoichiometric fuel oxidizer ratio. What does it mean that the amount of fuel either the amount of fuel is less than the stoichiometric requirement or the amount of oxidizer is more than the stoichiometric requirement. So, in both the cases all the fuel will be burnt some oxidizer will remain. So, such a condition is called fuel lean.

And on the other hand if phi is between 1 and infinite that is phi is greater than 1, in that case either fuel is more than the stoichiometric requirement or oxidizer is less for example, is this one or oxidizer was less. In this example what happen we had some unburn fuel remaining.

So, when this happens that when the equivalence ratio is more than 1 some fuel will remain unburn. So, that is called fuel rich. So, this is something that we will be using very frequently it is a good way to represent the overall ratio of fuel and oxidizer. Now, another parameter that is used many times is a little modification of this equivalence ratio.

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This is usually used for computational purpose is a parameter given by gamma hash, if you defined as fuel oxidizer ratio, actual fuel oxidizer ratio divided by fuel oxidizer ratio plus the stoichiometric field oxidizer ratio. Now, what is it is very similar to equivalence ratio, but typically it is used for computational purpose. Now, why is that? So, lets us understand. Here the resize is unbounded right. So, when we have pure fuel resize is unbounded equivalence ratio goes to infinity. So, computationally it cannot be handled where as if I look at gamma when we have lean then this gamma hash is bounded between, because for stoichiometric this becomes f naught.

Stoichiometric this is also size 1 by 2 right. Now, my stoichiometric condition which was for equivalence ratio 1, if selects as equivalence ratio with this parameters half. So therefore, for this is the bounding value. And for stoichiometric so for stoichiometric we get this equal to half for reach side on the other hand it is bounded between 0 and 1 right. So, this is the advantage it is bounded between 0 and 1. So, it is easier to handle numerically. And similarly for computational purpose you order to represent the entire mixture field or the entire field of species we defined another parameter, which is called mixture fraction.

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Let us consider a system like a rocket, where I have two propellants let us say oxidizer and fuel given here by A and B coming at certain amount. Let us say f k g per second of a is coming and they are what is going out is C, let us say 1 k g per second is what is going out.

Therefore, from conservation of mass the amount of B is essentially 1 by f k g per second right, it has to be bounded. So, a mixture now, we have the mixture here is flowing in this side just flowing at with a mass of 1 k g per second. So, this mixture now, C contains f k g per second of A and 1 minus f k g per second of B. Then any extensive property zeta of this mixture can be written as f times zeta A plus 1 minus f times zeta B equal to zeta of the mixture C. Therefore, I can define this f as zeta m sorry, zeta C minus zeta B by zeta A minus zeta B. So, this is called mixture fraction. This is something also when we have a very complex system of many many molecules we define in terms of mixture fraction. This is the very important toll.

So, with this we comfortable discussion on various representation of the fuel and oxidizer how much amount there are coming in. Now, lets us look at something else, what happens in the chemical reaction, when we have a chemical reaction. It can be exothermic so some heat will be liberated; it can be endothermic so some heat will be absorbed. Typically for chemical rockets what we are looking at, the chemical reaction are all exothermic, the release heat. So, then first of all how do we estimate how much

heat will be released, when we have two propellants coming and react. So, that is the thing we are going to talk about next. We are we are going to talk about heat of reaction, but before we go to heat of reaction, we will talk about something else, which is called heat of formation ok.

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So, let us now look at going to we have seen that in thermo dynamics courses I am sure, but let me just define the heat of formation. We defined standard heat of formation is given as delta H f naught units joules per mole. So, by definitions it is defined property. So, the standard heat of formation is the heat evolved, let me write it, heat evolved when one mole of the substance is formed that is why it is called heat of formation from its elements in their respective standard states at standard temperature and pressure.

Now, let us see what I am saying by this. First of all it is the heat evolved. Secondly, one mole of substance is formed, we are forming one mole of a particular substance. Thirdly it is form its elements in their respective standard state. And fourthly at S T P, standard temperature and pressure, first of all what is standard temperature and pressure, we consider in chemistry, it is 298.15 Kelvin and 1 atmosphere pressure, one bar pressure roughly that is the standard pressure.

Now so first we have define the standard temperature and pressure this is the state or condition at which we need to form the molecule. Secondly, respective standard states what does that mean, you know that anything can have three phases it can be gas, it can

be liquid, it can be solid. When we say the respective standard state it means that species what is this natural state as standard temperature and pressure. For example, let us say hydrogen, hydrogen appears in his natural state as hydrogen molecule H 2 right, in gaseous form right. Where as in cryogenic rockets you cool hydrogen to a much lower temperature that then it becomes liquid right, but liquid is not a standard state its standard state at S T P is gaseous.

So, this respective standard states means either it is gas or a liquid or a solid. For another example carbon, if I look at carbon C is at standard temperature and temperature solid. Therefore, carbon in a standard state is solid. So, what we are saying it as standard state from its elements one mole of particular molecule or substances fall when the heat evolved in this process is called heat of formation. It can also be stated as the enthalpy that is why I have written delta H, delta it is the enthalpy of this substance in its standard state. In reference to its element in their standard states at the same temperature. So, every element for example, let us look at water vapor, what are the elements present in this water vapor, we have hydrogen and oxygen tow atoms, those are the elements. So, to in water vapor is produced by hydrogen and oxygen at a standard state.

Then the heat evolved to produce one mole of water vapor is called heat of formation of water vapor. So, it can also be said that the enthalpy of water vapor heat of formation is enthalpy of water vapor at standard temperature and pressure minus the enthalpy of hydrogen and oxygen it is standard temperature and pressure is the heat of formation of water vapor. So, here the subscript f represents the formation and the super script o represents the standard state. By convention each elements in its standard state is assigned and enthalpy of 0. So, each element the way they appear in nature is assigned a standard enthalpy of 0 at a standard state. Or we can say that the standard heat of formation of an element in its natural state is 0.

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For example, if consider hydrogen, the heat of formation of hydrogen, because it appears as hydrogen like this in nature is 0. So, heat of formation of hydrogen is equal to 0. Similarly heat of formation of oxygen is 0 and because they appear as oxygen molecule in nature.

So, by convention each elements in the standard state is assigned an enthalpy are 0 or as a standard heat of formation of 0. Heat of formation of different element at tabulated extensively in the hand book of chemistry you can find various books and hand books in chemistry and physics where then tabulate this. Lets us now, look at how do we estimate heat of formation for a complex molecule little complex molecule not very complex. Let us look at carbon dioxide, what is the heat of formation of carbon dioxide. So, carbon dioxide what are the elements here carbon and oxygen. So, carbon dioxide can be form by through this reaction right, if you burn carbon pure carbon in oxygen environment pure oxygen environment then you get carbon dioxide carbon in its natural state is solids. So, we are talking solid carbon. Oxygen is natural state is gas so we are taking gas is oxygen.

And we will producing gaseous carbon dioxide. So, this is the reaction this is the formation reaction because we are forming one mole of carbon dioxide by burning one mole of carbon in its natural state which is solid and one mole of oxygen molecule which is a natural state. So, the heat evolved here in this reaction is equal to minus 94.054 kilo

calories per mole. So, this is then the heat of formation of carbon dioxide at the standard state. Now, another convention here we see that this is negative, this heat of formation is coming with negative value. So, the convention says that when heat is evolved in the formation of a compound that is heat is coming out, because of the chemical reaction. Then delta H f is negative if the formation reaction is exothermic delta H f negative.

So, if exothermic reaction delta H f naught is negative and for in the reverse for endothermic reactions delta H f naught is positive. So, essentially what it means is that in this formation reaction heat is liberated where as in this formation reaction endothermic formation reaction we need additional energy from outside to carry forward the change. Now, delta H f naught for exothermic reactions are negative, because heat must be taken away from the system.

So, what is happening is that if I take a system, let us say have carbon and oxygen here and carbon dioxide is formed, let us say consider a close system. Now, and the reaction happens this heat amount of heat is produced. Now, this is a close system if you do not take away this heat the temperature is going to increase right. So, we take away some amount of heat delta H to maintain the constant temperature. So now, what is happening, the system is losing heat that is why it is given as negative. On the other hand in endothermic reaction in order to maintain the constant temperature we have to supply from outside right.

So therefore, that becomes positive, because in chemical equilibrium and chemistry the convention is that heat added to the system is positive, it taken from the system is negative. So, that is why this convention. So, a substance with a large positive standard heat of formation tens to be a more chemically active species, this is something we have to know. Now, this is how where we have defined now heat of formation. The question is how do we use this information, we get the heat of formation, but most of our chemical reactions are not formation reactions there are much more complex than that. So, how do we use this information that, if you know the heat of formation how do we get to know that in a complex chemical reaction, how much heat will be produced for that we need some more other thermo chemical loss. So, let me talk about couple of modes and chemical loss.

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This is the law why Lavoisier and Laplace. This was proposed in 1780, the thermo chemical law. This law states that the quantity of heat, which must be supplied to decompose a compound into its element is equal to the heat evolved when the compound is formed from its elements.

So, what does it say that, if I take a compound let us say once again carbon dioxide. And I want to break it to carbon and oxygen then the amount of heat will be required to break this carbon dioxide molecule into solid carbon and gaseous oxygen is same as the amount of heat that evolved when carbon dioxide was formed from this two that is what this statement says. So, the general form of this law can be said is that the heat change accompanying a chemical reaction in one direction this is one direction right, is exactly equal in magnitude, but opposite is sign if we have reaction in the other direction. So, learn here what is happening this was why my reaction right.

So now, if we have to go from here to here we need to add this amount of energy, this magnitude of energy to get this thus the general statement or general form of this law. That the heat evolved in forward direction is equal to the heat evolved in the backward direction magnitude is same, but the signs will be different. So, for example, it will look at an example gaseous methane burning with oxygen again gaseous giving C O 2 plus 2 H 2 O, let us say liquid form. So, this is the exothermic reaction.

So, the heat evolved is 212.8 kilo calorie if I look at the reverse of this reaction C O 2 gas plus 2 H 2 O liquid. So, I take carbon dioxide gas and liquid water and supply this amount of heat, I should be able to get theoretically, I should be able to get methane and oxygen back. Now, look at this carbon dioxide with water giving methane and oxygen. So, we are getting fuel out of carbon dioxide this is something, if you can do it efficiently can be great they are producing oxygen. Similar thing like this happens actually in photosynthesis when the plants absorbs carbon dioxide use water and not methane it gets higher they will loss etcetera and oxygen right. So, this is similar to what happens, but that requires energy.

So, if we can provide the amount of energy and conduct the reaction properly, theoretically we should be able to get fuel out of carbon dioxide and water vapor, but unfortunately we are still not been able to do that. So, here both this reaction will occur at the same temperature, standard temperature. So, this is what the general thermo chemical reaction means, I will stop here today. I think we are out of time. I will stop here today. In the next class I will continue with one of thermo, another thermo chemical reaction and then we go into the estimation of heat of reaction.

Thank you.