

Rocket Propulsion
Prof. K. Ramamurthi
Department of Mechanical Engineering
Indian Institute of Technology, Madras

Module No. # 01
Lecture No. # 16
Choice of Fuel-Rich Propellants

Good morning. I think we will continue with chemical propellants in this class namely, the criterion for choice of propellants which are essentially chemicals with which we are concerned. What did we learn so far? We told ourselves all the propellants, all the chemicals which are used as rocket propellants must have low atomic mass, such that we have low molecular mass of products point 1. Point 2 we also told ourselves may be it must be dissociated. What do you mean when I say that the products of combustion must be dissociated? Instead of having water if I could have something, like H atom or O atom or OH atom, well the specific heat will be smaller. Therefore, the temperature will be larger. Maybe I will take a look at it subsequently may be in the next class.

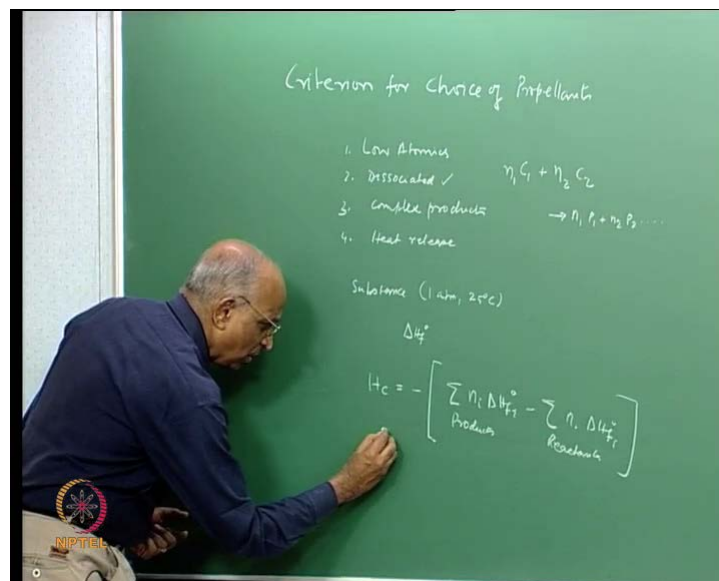
Third, we told ourselves from gamma point of view, it may be better to have more complex products of combustion. This complex product is against what we decided here and towards the end of last class, we also defined when the heat release from combustion, heat release from chemical reactions of these propellants and we defined the term heat of formation. What did we say heat of formation is? We told ourselves, heat of formation relates to a substance which we are interested, may be the heat required to form the substance at the standard condition, standard condition being one atmosphere pressure and say 25 degree centigrade. This is the standard condition.

The heat required to form the chemical or the substance at these standard condition from the elements which constitute the substance again at the standard condition, we define as heat of formation. This is the way we use it for products, for chemicals, anything what we require. Therefore, what is the heat which is released in a chemical reaction, we told ourselves. I will write in a little different way. If I have products and the sum of the products, the heat of formation of the products, let us say products consists of n_1 moles of n_1 , n_2 moles of the second substance and so on and each of these substances have a heat of formation, standard heat of formation which is given by Δ_f

corresponding to its substance. I have heat of formation of the substance. Well, this defines the heat of formation of the products.

Now, I subtract from it the summation of heat of formation of the reactance again. I say I have substance heat of formation at the standard condition for the reactance and then, if there is a decrease in the heat of formation, I say some energy is released in the combustion. Let us be clear about this notation what am I telling here. I have in the reactance. I have let us say the chemical one having one mole may be n_2 moles of chemical 2 forming, let us say n_1 moles of product one plus n_2 moles of product 2 and so on. All what I say is $n_1 C_1 + n_2 C_2 + \dots$ going from 1 to 2 for the reactance. I going from 1 to n for the products and this is how we are seeing is the heat of combustion.

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What do we want? We want this heat or which we also called as q to be as large as possible and for this, we looked at heat of formation of certain substances, we looked at heat of formation of let us say methane, ethane and so on, propane, butane and all that up to kerosene which we called as dodecane $C_{12}H_{26}$. We found that the heat of formation keeps increasing in the negative direction for this series of hydrocarbons. Therefore, we told ourselves if the substance or the chemical is little more complex, may be the heat of formation is higher and this we also saw in the example when we saw CO_2


and when we saw CO. We found that the heat of formation of CO₂ was something like almost 386 or 387 kilojoules per mole whereas, CO we found it was 100 and 100.5.

In fact, we use the reaction to find out the heat of formation of CO, heat of formation of CO₂, little more complex means the heat of formation is higher. Mind you it was negative 387 minus 100 and 5.5 kilo joule per mole. Therefore, we would like to know for a chemical to produce maximum heat release. What should be the choice of heat of formation of the substance, that is what I am trying to get it and this is the only thing which is left. Once we do that may be we will be a little bit wiser in the choice of propellants to be used for as rocket propulsion and that is what I am trying to do.

Let me get back to the slides here. What I have shown here is for fuel say, methane minus 75 ethane minus 85 propane minus 104 butane. See it keeps on increasing and till we come to kerosene, it has increased and it is a negative quantity. That means increasingly negative quantities.

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HEAT OF FORMATION	
FUELS	EXPLOSIVES
CH ₄ : -74.9 kJ/mole	N ₂ H ₄ : +50.3 kJ/mole
C ₂ H ₆ : -84.7 kJ/mole	NC: -670.6 kJ/mole
C ₃ H ₈ : -103.9 kJ/mole	
C ₄ H ₁₀ : -124.7 kJ/mole	
C ₁₂ H ₂₆ : -292.9 kJ/mole	
POLYMER: -80 kJ/mole	
H ₂ : 0 kJ/mole	



If I have a polymer, what is a polymer? Polymer is a slightly different animal, in the sense we are looking at something like a chain which consists of may be c x h x o c x h y o is 8 and it keeps on as change may be m times. It keeps on qualifying like this. We find that the heat of formation of some of these polymers and we will look at polymers in some detail like poly butadiene and all that. When we deal with solid propellants, these have a heat of formation as shown in this slide as something like minus 80 kilo joule per

mole. When we talk of other fuel like hydrogen, well hydrogen at the standard condition is an element and therefore, the heat of formation is 0. I think for different fuels, we therefore say well, for hydro carbon fuels, it keeps increasing as the complexity of the substance increases for a polymer. It is around, let us say minus 80 kilo joule per mole for hydrogen which is an element and again at the standard condition, it is 0 kilo joule per mole. Is it clear?

Now, I want to also define some more substances. In the last class, we told there are some substances which are known as explosives. We keep on reading about explosions here and there. What is the difference between explosive and a fuel? When we have fuel and oxidizer already mixed together, premixed very well or if not premix, it is a form of a molecule itself. That means fuel and oxidizer are an integral part, either extremely well mixed or else it is a part of the substance itself.

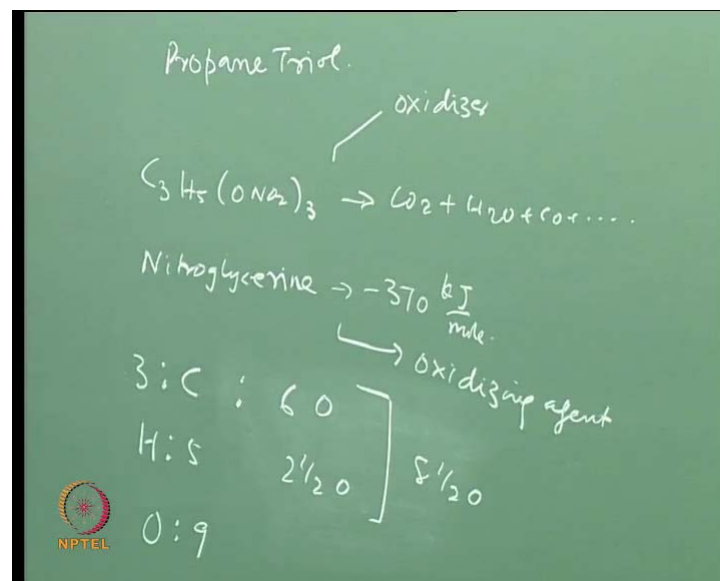
Let us take one or two such explosives and that will be very instructive. In the last class, I started with nitroglycerin. When we say nitroglycerin, it is basically we are talking of glycerin and glycerin is derived from propane. In propane what you do is you take C_3H_8 which is propane. You take 3 of the 8 h atoms, substitute it by oh. That means we have $C_3H_5OH_3$. This becomes something like 3 of oh. This is known as propane triol. That means it is just an alcohol of propane. Now, in this you take the oh out. You substitute oh instead of substituting, instead of o h; you put something like a nitro radical. You put $C_3H_5ON_3$ times and this becomes nitro based on glycerin which is propane triol and this is known as nitroglycerin.

This as a heat of formation as shown here may be in the next one you see that the heat of formation of nitroglycerin is around minus 370. How do you get it? You do an experiment. You find you have minus 370 kilo joule per mole, but why did I take this particular expression of nitroglycerin here. I want to know whether nitroglycerin can act as an explosive. It has oxygen, it has fuel, it can burn together to give me let us say CO_2 plus H_2O plus may be CO may be any of the things it could form, but if I look at the substances which are there in nitroglycerin, I find it has 3 of carbon. If it take hydrogen, it has 5 of carbon, 5 atoms of carbon, 3 atoms of I am sorry, 5 atoms of hydrogen, 3 atoms of carbon and if I take O here, it has 3 3 O as 9. That means it has 9 atoms of oxygen, 5 of hydrogen, 3 of carbon.

Now, if I want to oxidize the carbon, I need something like 6 atoms of oxygen to form CO₂. If I want I want something like two and half atoms of oxygen to form CO, two and half atoms of oxygen to form or two and half. Why even less I have 5 atoms of hydrogen. Therefore, I have two and half of O is all what is required. 6 of O to form let us say carbon-dioxide. I think I should repeat this again.

I think this part will be clear in nitroglycerin molecule. I have 3 atoms of carbon, 5 atoms of hydrogen and 9 atoms of oxygen. If I want all the carbon atoms to form carbon-dioxide, well I need something like 6 O. If I want to oxidize all the 5 atoms of hydrogen to form water, well I need two and half and therefore, all what I require for complete oxidization is eight and half O, but I have 9 O. Therefore, nitroglycerin could help, could still act as an oxidizer even though it is an explosive. It has still balance oxygen left which can still be used for oxidizing and nitroglycerin we say is an oxidizing agent.

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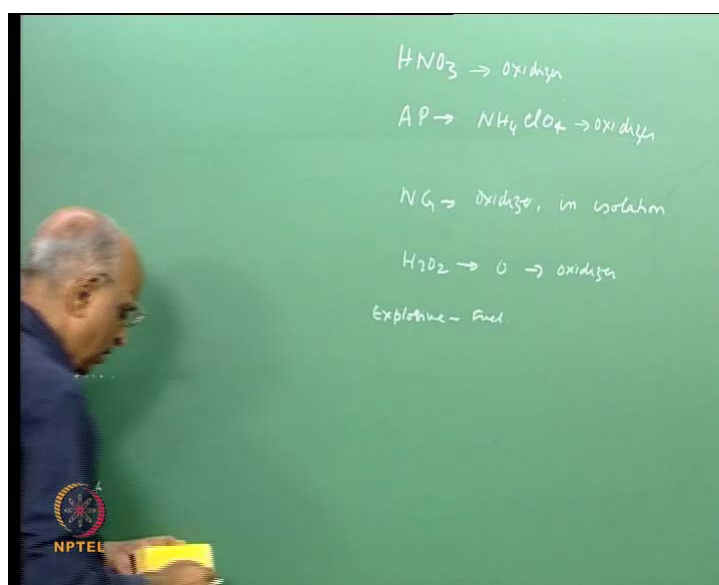


I think I should repeat it because it is something which is important. Let us take a substance like HNO₃ nitric acid. If I take nitric acid, you know I have one atom of hydrogen which requires half atom of oxygen. Therefore, I am still left with two and half atoms of oxygen. Therefore, nitric acid can be used as an oxidizer. That means it can still be used as an oxidizer even though it is an acid.

If I have a substance like ammonium perchlorate, all of you would have heard of it. It is a very widely used oxidizer for solid propellant rockets. The formula is ammonium

NH_4ClO_4 . Well, I have 4 atoms of oxygen, but I have 4 atoms of hydrogen requiring only 2 atoms of oxygen for oxidization. I have chlorine which is again oxidizer. Therefore, it can also be used as an oxidizer. Similarly, if I have nitroglycerin, nitroglycerin can react by itself. I can use it as a propellant directly, but I can also use it as an oxidizer in combination with some other fuel and still I can use it as an oxidizer or else I can also use it in isolation as nitroglycerin itself.

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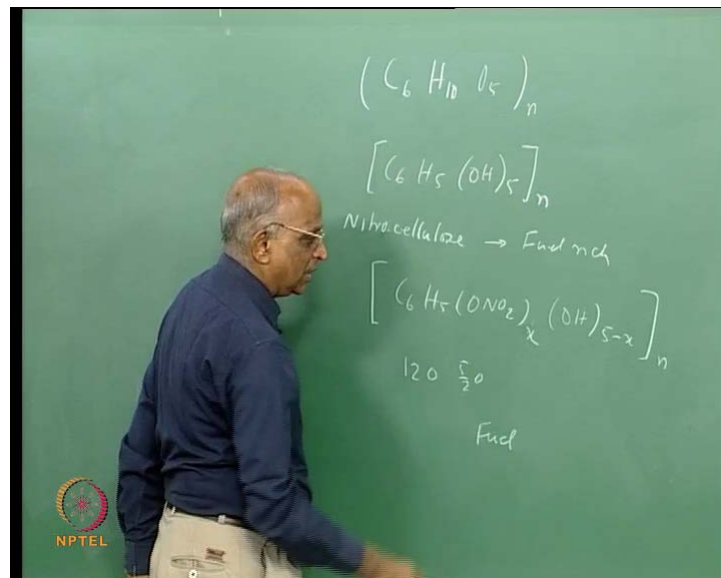
Similarly, if I take something like H_2O_2 which is hydrogen peroxide, you know I do not need all the O to form water. I am left with one O and therefore, H_2O_2 can also act as an oxidizer. Mind you H_2O_2 is an explosive, nitroglycerin is an explosive. All these are all substances, but some of them even though they are substances in which fuel is there, it can still act as an oxidizer.

Therefore, let us take one example of a fuel you know is stated with nitroglycerin which was an oxidizer. Let us take an example of a fuel which is an explosive, an explosive which can act as a fuel. The simplest one is may be this wood which is cellulous, what I take is if I take the formula for cellulous, you know cellulous as a molecular formula $\text{C}_6\text{H}_{10}\text{O}_5$ and it consists of this in several places like n times. It gets repeated like we will have $\text{C}_6\text{H}_{10}\text{O}_5$, again $\text{C}_6\text{H}_{10}\text{O}_5$ and so on and number of times and this is how cellulous or paper is made of.

Now, we can also write this above formula as I can write it as C₆H₅ into OH₅. Therefore, I say yes it consists of a number of these molecules together may be n of them together. Well, this is the equation to cellulose or formula to cellulose and suppose, I want to nitrate it. That means I want to make nitro cellulose. I take some of the OH over here, substitute it by ONO₂ and what I get is may be part of them. Not all 5 in the molecule, I get C₆H₅ on O₂. I take x of t 5 over here and the balance OH is still available as 5 minus x and this is to the power to n number of times this gets repeated.

Now, what is it we have done? We now have the formula for nitrocellulose which is now C₆H₅. We nitrate on O₂ x x times and OH₅ minus x times. Now, if we look at this, you know C₆ carbon 6 of them requires O₂. That means I need 6 of oxygen. That means 12 of oxygen atoms H₂O, this requires 5 by 2 of oxygen atoms because H 2 is what is formed and then, again I have h over here which requires more oxygen, but the oxygen which is available is only 1 plus 2 3 x times and here, O₅ minus x is always available. Therefore, the availability of oxygen in nitrocellulose is much lower than the amount of carbon and hydrogen which is there.

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Therefore, in a sense the oxygen available within the molecule is much less than the fuel component of carbon and hydrogen. Therefore, nitrocellulose we say is fuel rich. It can dissociate by itself using the small amount of oxygen, but it cannot form completely oxidized species since carbon and hydrogen are more than the oxygen available and

therefore, it is also used as a fuel. I use it as a fuel because the component of fuel in the nitrocellulose is much greater than the amount of oxidizer in it and this nitrocellulose if you were to go back and look at what is the heat of formation, it has a large negative value which is minus 670. We talked of N_2H_4 the other day. Hydrogen which is again an explosive which is plus 53, therefore you have all these substances may be including an explosive which could act as a fuel and these are the heat of formation of the different fuels. Therefore, you see the heat of formation fuels varies from something like a positive number of plus 50 to a large negative value of minus 670 and it still keep varying.

Now, we go back and take a look at what is a heat of formation of the oxidizers. Well, an oxidizer now I can go a little faster. Oxidizer could be oxygen. Oxygen is an element at standard condition. The heat of formation is 0. If I have nitric acid, well it is an oxidizer. It is minus 171. If I remove h from it and if I make into something like di nitrogen tetra oxide into a 4 which is again a volatile liquid, I get something like plus 90.63 kilojoules per mole. I talk in terms of other oxidizers solid ammonium perchlorate which I just now said NH_4ClO_4 . NH_4Cl_4 over here, it could it has a heat of formation of something like minus 295. If we instead of the perchlorate radical I use the nitrate radical, NH_4NO_3 have the heat of formation minus 365.

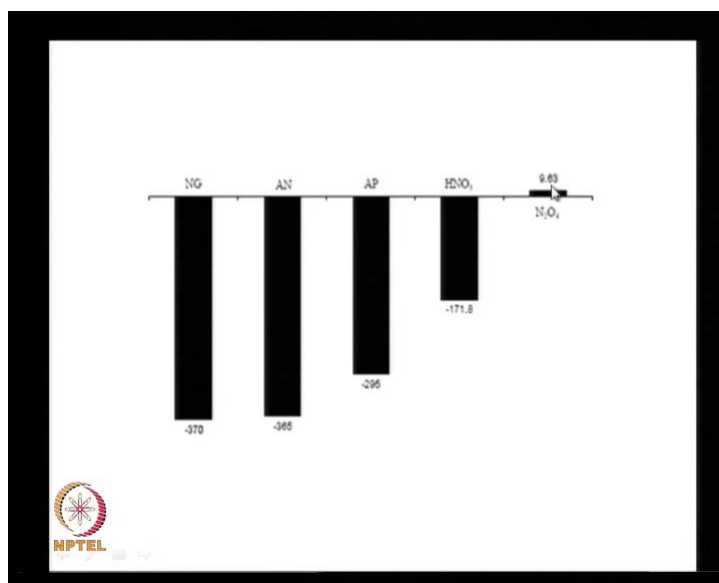
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HEAT OF FORMATION	
OXIDIZERS:	EXPLOSIVES
O_2 : 0 kJ/mole	N_2 : -370 kJ/mole
HNO_3 : -171.3 kJ/mole	H_2O_2 : -187.8 kJ/mole
N_2O_4 : +9.63 kJ/mole	
AP: -295 kJ/mole	
AN: -365 kJ/mole	



Therefore, you see the heat of formation also widely varies and for certain explosives like nitroglycerin is minus 370, for hydrogen peroxide it is minus 187. Therefore, I tried to put all these things together just to get a feel for the problem. Well, nitro nitroglycerin as a large negative value N2O4 as a slight positive value and this is the variation of this between minus 370 to something like 9. This is for oxidizers.

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Similarly, for other substances which are the products, what are the products we have been handling, we have been telling? Well, carbon gets oxidized to CO₂ or CO may be the hydrogen gets oxidized to H₂O. Therefore, the products are essentially CO₂, may be CO, may be H₂O and so on. If I have aluminum in the metal, I could form aluminum oxide and these are some of the products which we are interested and if you look at the heat of formation of some of these things which we worked out in class again, it was something like CO₂ as minus 391 kilo joule per mole, CO as minus 110 water as minus 296. Mind you this is important.

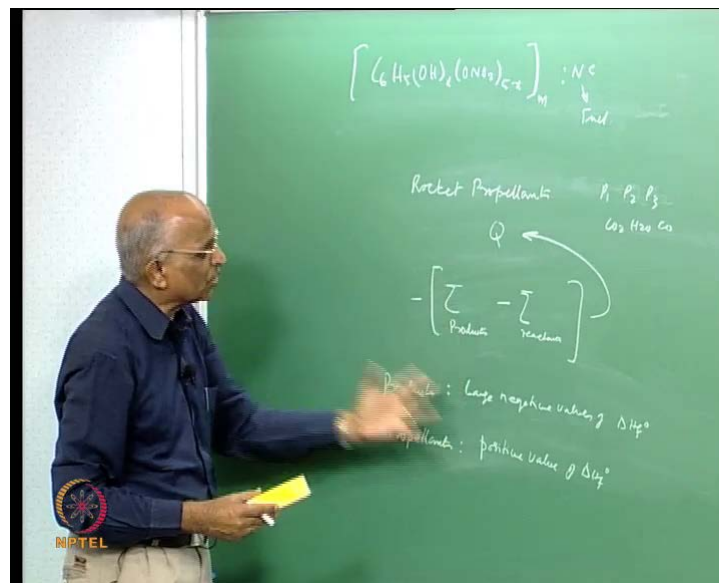
When I say water, why is it water? Because I am looking at the standard condition of 25 degree centigrade and at that pressure is not that important for a liquid. Therefore, under standard condition, it is water. Therefore, the water has minus 296 H dissociated we found it is plus 217 OH dissociated is again a high value 395, but if I take aluminum oxide, it is extremely large negative value minus 1670 kilo joule per mole. Well, these

are some heat of formation which is given to you. How do you get it? They do experiments give the heat of formation.

Now, why is it we are interested in we would like to have propellants or rocket propellants or chemical propellants? Rocket chemical propellants which will give as much q as possible and to be able to get high value of q , we just now told ourselves, well the products net heat of formation minus net heat of formation of the reactance minus is what gives me the value of q . Therefore, what is it I see from this if the products could have individually negative values and if the products could have high negative values, then this negative and this negative becomes positive. I could have high value of q .

Therefore, one of the requirements of chemicals which can be used as propellants is they must have large negative values of heat of formation. Mind you when I say products, by products I am not talking of chemicals. I am talking of may be p_1 p_2 p_3 or rather I am looking at CO_2 , H_2O , CO . What are the products formed? The products must have I should write this as products having large negative values of heat of formation. Is it ok?

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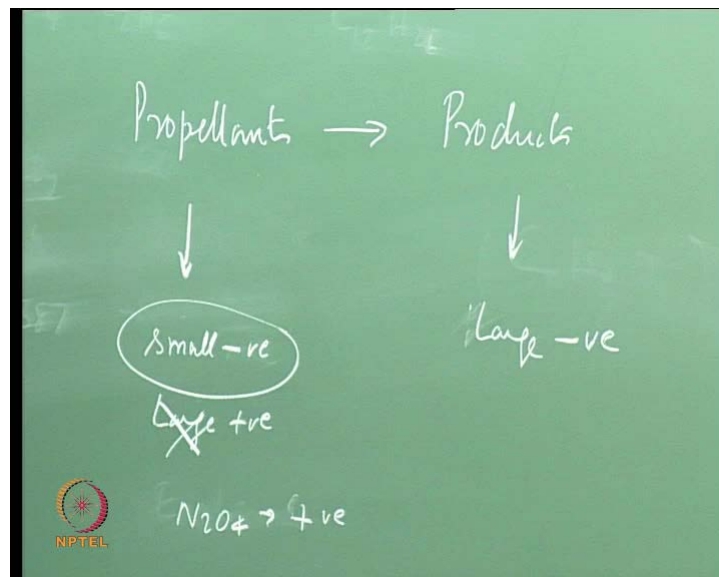


Similarly, if I talk in terms of the reactance which are essentially the propellants, what should they have minus and minus becomes plus. Therefore, if the reactance would have positive value of heat of formation, it is better for me because I have a more positive number. Therefore, based on this logic, all what we say is if I have something like propellants, let us put it down again. If I have a single chemical or a single substance

going propellant may be or a combination of propellants giving me something like products, the products should have large negative values whereas, the propellants must have small negative or better to have large positive value.

Why did I write small negative values? It is because if the heat of formation is positive, the substance is basically unstable. Why is it unstable? Because you are supplying so much heat to form the substance that it cannot remain so in the standard condition. Therefore, the general thing is why it should not have a small negative value instead of a large positive value which is not possible.

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In general, some of the substances like N_2O_4 have small positive value; some of the explosives have positive values. We will consider these explosives earlier, but in general, most of the substances like kerosene or other substances have negative values, but the desirable feature is a propellant should have large positive value because large positive value makes these substances unstable. We sort of compromise and tell ourselves well, a small positive value or a small negative value is all that a propellant should have. This tells us what is the choice from the heat of formation point of view and this is all what we are required to know about choice of chemical propellants.

Therefore, if this part is clear, may be subsequent things are quite simple. Therefore, we tell ourselves the choice of propellants for rockets basically should have propellants

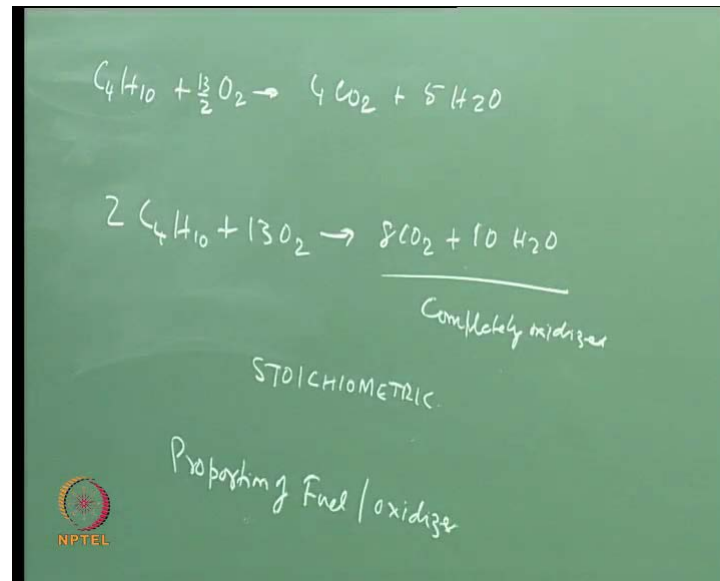
which have positive value of heat of formation or small negative values and the products they form should have large negative values. I think this part must be clear.

We will do one or two problems towards the end of this class. It will become further clear, but question is if I have let us say propellant like let us say, I consider a propellant like butane, but unfortunately, butane is a gas and it is difficult to use, but let us take this example plus I have oxygen as the oxidizer. Butane has the formula C_4H_{10} plus oxygen. Let us say, it completely burns into carbon dioxide, therefore I get 4 CO_2 plus I have H_2O . Therefore, I get 5. Now, I want to balance this reaction, therefore I find 4 8. Therefore, I have 8 of oxygen plus 5 13. Therefore, I get 13 by 2 of oxygen.

So, I can write this reaction as C_4H_{10} multiplied by 2 2 C_4H_{10} plus 13 O_2 gives me 8 CO_2 plus 10 H_2O . What is this reaction? In this reaction we form completely oxidized products of combustion. I cannot oxidize water. More than water I cannot oxidize carbon dioxide further than this. Therefore, these are all completely oxidized products, completely oxidized and when we form a reaction in which the products are completely oxidized, we call the reaction to be stoichiometric.

What do you mean by stoichiometric reaction? The proportion stoichio means element and metric means proportion in Greek. Therefore, we are talking proportion of the fuel and oxidizer such that we form completely oxidized products of combustion. This is what we mean by a stoichiometric reaction, but the question is if I have butane as a fuel, as a rocket propellant oxygen, as an oxygen, as an oxidizer, what is this? Is it possible that the variation of stoichiometric instead of having something like a 13 of oxygen, 13 moles of oxygen for every 2 moles of butane will something like 15 moles of oxygen given me better value of c^* or better value of temperature or better value of heat release. Will that be better? In other words, I would like to consider proportion of fuel and oxidizer what I require.

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When we studied the subject of combustion, we talked in terms of equivalence ratio, fuel air ratio and we said equivalence ratio is fuel air divided by fuel air under stoichiometric, but in rocket tech parlance or the terminology used in rockets, we use the word mixture ratio and mixture ratio is defined as mass of oxygen or mass of oxidizer divided by mass of fuel in a chemical reaction.

Let us illustrate it. I deliberately took this example. If I want to find out what is the mixture ratio of this stoichiometric reaction, what is the mixture ratio, let us put it down. Can we do it? Mixture ratio for stoichiometric combustion of butane with oxygen is equal to mass of oxygen is 13 into 32. The amount of fuel is 2 into 124 plus 10 which is equal to 13 into 32 divided by 2 into 58. Is it all? That is the mixture ratio for this reaction is something like 3.6. Therefore, if I use a fuel in the proportion oxygen to fuel in the proportion 3 to 3.6, I get completely oxidized products of combustion.

Now, I take another example. How do you calculate the heat release? All what we do is the heat release for this reaction is equal to 8 into minus the value of CO₂ was something like 386. How much was it heat of formation? Let us go back. It is in front of us. 397 plus I have 10 into water. Water is minus 286 minus the heat of oxygen is 0 as an element butane is slightly lower. I think it is minus 105 minus 1204.7, that is 2 into minus 1204.7 is the heat liberated in this reaction for 2 moles. I am getting this amount of heat.

Therefore, this becomes the decrease. I have to look at this is the heat of formation of the products, heat of formation of the reactance. I am going to say how much this has decreased. Therefore, this is minus. Therefore, I get 8 into 397 plus 2860 minus 2 into 1204.7 so much kilojoules of energy which is liberated and this is how we calculate the heat liberated in this stoichiometric reaction.

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The image shows a green chalkboard with handwritten mathematical calculations. At the top, the mixture ratio (MR) for a stoichiometric reaction is calculated as $\frac{13 \times 32}{2[48+10]} = \frac{13 \times 32}{2 \times 58} = 3.6$. Below this, the heat of reaction is calculated as $- [8 \times (-397) + 10(-286) - 2 \times (-124.7)]$, which simplifies to $= 8 \times 397 + 2860 - 2 \times 124.7 \text{ kJ}$. In the bottom left corner of the chalkboard, there is a small circular logo with the text 'NPTEL' underneath it.

Suppose, instead of having stoichiometric composition, I take let us say I put extra oxygen into it like I say I take oxygen amount as 15 instead of 132 C_4H_{10} plus I have 15 O_2 giving me again. What is this reaction going to give me? I have excess oxygen, therefore I still get 8 CO_2 plus I get 10 H_2O plus I am left with 2 of oxygen. Is it because I have more oxygen than available? The oxygen first oxidizes the carbon and the hydrogen to form carbon dioxide and water and this is what I get.

What is the mixture ratio for this reaction? It is equal to I get 15 into 32 mass of oxidizer mass of fuel 2 into 508. We just now said it is 48 plus 1058 and this gives me a value of as something like 4.14. How do I get? That means the mixture ratio has gone up from 3.6 to a value of 4.14 and that is the heat release in this reaction is this going to be different from that one. It will be same because oxygen here has nothing. Therefore, the heat of reaction is still at the same value over here.

Let me consider the third one in which I consider in which case I have less of oxygen available. I take the same reaction to C_4H_{10} plus now I say instead of giving 13 for

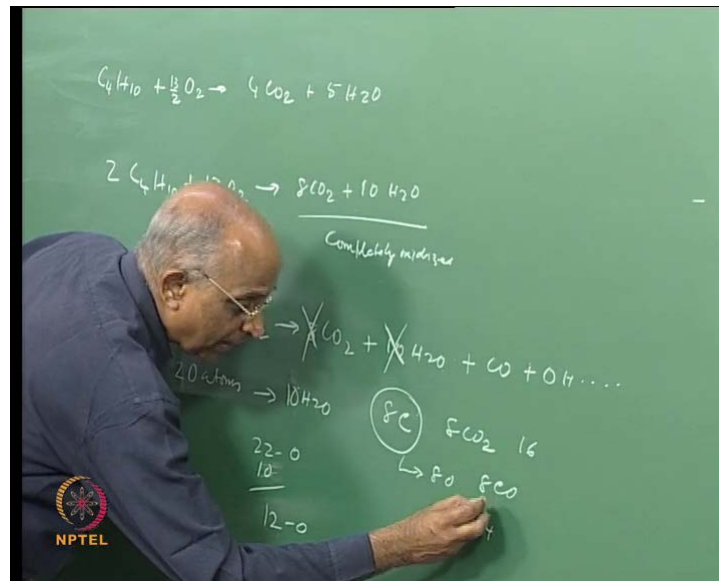
stoichiometric, I give 11 of oxygen. That means I am stopped for oxygen. If I am stopped for oxygen, what is going to happen? You know I cannot get all CO₂, I cannot get 8 CO₂, I cannot get 10 H₂O. The reason being you know if this is there, I need 16 plus 20. That means 26 whereas, I have only 22. Therefore, this is not possible or this is not possible somewhere I have to balance it.

One of the ways which we could do is to be able to find out that means I cannot get all carbon dioxide, I cannot get all water. May be I am going to form something like CO. I am going to form OH and other substances because there is inadequate oxygen to form carbon dioxide and water.

Now, how do I determine this? I cannot just like this determine. I would have to do an analysis for the equilibrium composition of the products at a given pressure and temperature which means I have to use chemical thermodynamics to be able to determine this composition and that I will do in the next class, but before I do that, you know instead of doing the detailed dissociation and chemical equilibrium or equilibrium of the products is what we have to consider.

There is a slightly easy method of doing this problem. What is it? We say hydrogen is very reactive and therefore, all the 10 atoms of hydrogen, they search for oxygen and get converted into something like 5 H₂O, that is 10 pick up the 5 oxygen from here. I had originally 22 oxygen and I have removed 5 from here. Therefore, I am left with 17 oxygen and now, out of these 17 oxygen, what is going to happen to me. Yeah we have 20 atoms. Therefore, I have 10 H₂O if I have 10 over here, when I have 12 left. Was this your point? That means I have 20 atoms of hydrogen requiring forming 10 H₂O as it is here because hydrogen is very reactive I am left. Therefore, 12 atoms, but here I find I have 8 of 8 of carbon and therefore, I am left with 8 of carbon and I cannot form 8 of CO₂ because this will require 16 atoms of oxygen whereas, I have only 12.

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Therefore, what I do is I say well, I have 8 of carbon. Let me first use the 8 of O to form 8 CO and if I still form 8 of CO, I am left with again out of 12, 4 of oxygen and what I do is I use these 4 of oxygen to form take 8 of CO form out of the 8. I remove 4 and I form 4 of CO₂ and therefore, the reaction will now look like 2C₄H₁₀ plus 11 O₂ gives me first hydrogen. That means 10 H₂O plus I get 4 CO₂ plus 4 CO.

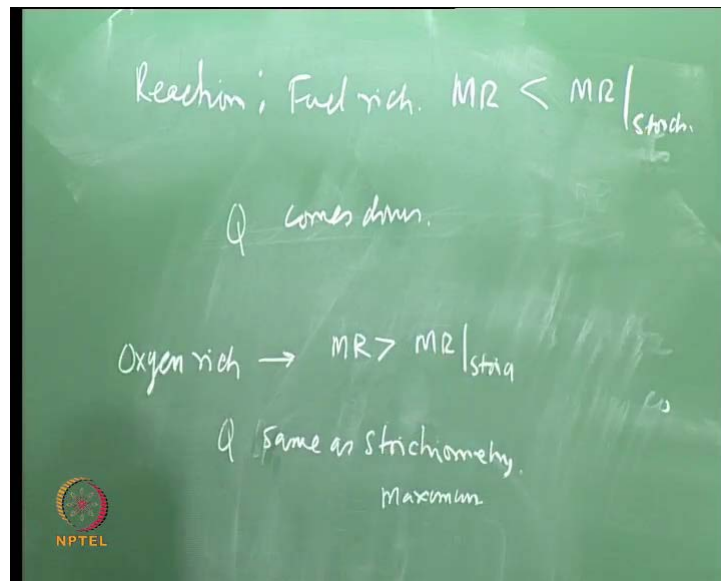
Let me repeat it. Some of you have done it in your explosive explosion course, but what we are telling is when there is insufficient oxygen, first the oxygen attacks the hydrogen because hydrogen is very reactive or rather the hydrogen removes the oxygen and all the hydrogen gets oxidized to form water. The balance of oxygen oxidizes the carbon to form carbon monoxide and still if some oxygen is left, the balance or the part of the carbon monoxide is converted to CO.

I think you all should practice this and therefore, you have a reaction wherein, now you get this done. What is the heat? What is the mixture ratio of this particular reaction? Mixture ratio of this reaction is equal to 11 into 32 divided by 2 into the value of 58 and this gives a number as equal to something like 3.03. What is the heat liberated in this reaction? The heat liberated in this reaction is minus of 10 into the heat of formation of H₂O plus you have 4 into this is the minus value plus 4 into this and minus of the total thing minus the heat coming over here. Is it going to be higher or lower compared to

stoichiometric? It will be lower because CO has a value which is minus 100 and 10 CO₂ has a higher value minus 297.

Therefore, you find that when a reaction is somewhat fuel rich, when a chemical reaction is fuel rich, that means, it is short of oxygen. The value of q comes down whereas, if it is oxygen rich, then q of combustion q is same as stoichiometric and this is the maximum heat which is possible in a chemical reaction.

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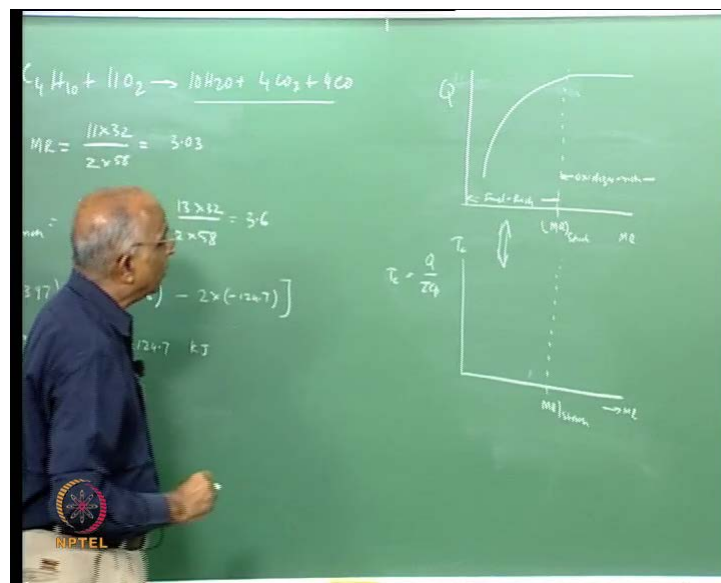
If this is so, I again ask myself the last question. Oxygen rich means the mixture ratio is greater than mixture ratio is stoichiometric fuel rich means mixture ratio less than mixture ratio stoichiometric. Is it now I want to plot this result? So, let us plot it out. We see our aim is to get a high value of temperature or we are still debating what must be the choice of the proportion of fuel and oxidizer to be used as rocket propellant.

So, now I want to plot this out. I say what is a heat release in a reaction? Suppose this is stoichiometric and I plot it as a function of mixture ratio and this value I call as mixture ratio stoichiometric. I find anything more than this gives me the maximum value of heat release whereas, below this I keep on dropping because unoxidized or not completely oxidized products of combustion are being formed.

Now, I want to convert it into temperature. How will I convert it to temperature? I tell myself well, this is the fuel rich part, this is the oxidizer rich part and I want to convert it

to temperature. How do I convert it? We calculated in fact the heat of combustion or the heat which is liberated in the chemical reaction by looking at the products heat of formation of the products. We said it must be less than the heat of formation of the reactance and that is the deficit of the heat which is generated. Therefore, if I were to divide it by the summation of the mole or specific heats, this will give me something like the temperature minus the initial. It will give me the combustion temperature. That means specific heat into the number of moles into the temperature increases the heat release.

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Therefore, T_c is equal to q by c_p and now again, I take the same thing, mixture ratio stoichiometric and this is mixture ratio scale. Now, this is the temperature scale. You know how should graph look like. Well, we still need to do something. Here, I have moles which are coming in. I need to be able to convert it because I will say per mole here, the number of moles are varying because in one case I have different number of moles and in the other case, I have different number of moles. A direct comparison from this to this might be little difficult, right. Therefore, what we could probably do is convert the heat release into heat release per mole.

Let us do that exercise. If you were to do that exercise and plot on a graph, maybe I will go to the left side q per unit mole or which is similar q per unit mass as a function of mixture ratio and then, I again put mixture ratio is stoichiometric. How will that curve

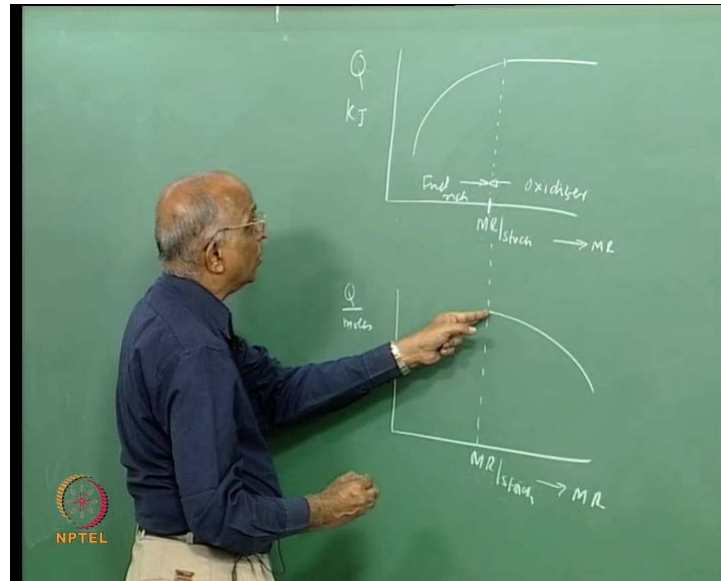
which was like this translate over here? Let us do this exercise. Let us again go back into these equations and see for stoichiometric. You have C_4H_{10} plus $13/22$ of this. When it was fuel rich, the number of moles increased and therefore, even though q is same as it become more and more oxidizer rich, what is going to happen? We plotted the heat release q so much kilojoules as a function of equivalence ratio or mixture ratio and the mixture ratio is at this corresponds to mixture ratios stoichiometric. This corresponds to the oxidizer rich because mixture ratio is defined as mass of oxidizer divided by mass of fuel. This is oxidizer rich zone and this is the fuel rich zone.

What is it? We found when the oxygen content was more than what is required for stoichiometric, the heat content does not change. In fact, it remains same whereas, in the fuel rich side, since we are not able to burn all the carbon and hydrogen atoms, the heat release keeps coming down. Therefore, we had got a plot of q verses mixture ratio. Here, it is mixture ratio, this is mixture ratio stoichiometric and we had got plot of heat generated verses mixture ratio to go up to the stoichiometric mixture ratio and thereafter remain constant, but let us take a look at this figure again.

Supposing, I want to plot. Instead of plotting q on this axis, supposing I want to plot q divided by the number of moles of products which are formed, then what is the type of behavior what I get to see. Ultimately, I am interested in finding out the temperature. Therefore, I want to find out for per unit mass or per unit mole, if I can divided by specific heat, I get the temperature and therefore, let us first find out what is the value of heat release per unit mole in the product.

Now, again I plot over here. This my axis is mixture ratio, this is mixture ratios documentary. Now, what is happening as the oxidizer quantity increases, I am left within the products with more and more of oxygen that is the number of moles in the product increases. Therefore, if this is the value of heat release per mole corresponding to this point, the curve begins to drop because the number of moles are increasing in the product.

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How about in this case? You know since it is fuel rich, I am not able to form that much of moles now. Therefore, the number of moles decrease and therefore, this curve would become a little shed over here rather the peak value of heat release per unit mole is still at stoichiometric and either side in the fuel rich side and in the oxidizer rich side, the curve begins to drop.

In other words, the amount of heat release per unit mole as a behavior which gives maximum at the stoichiometric mixture ratio and falls on either side of it, now instead of expressing heat release per unit mole, I can also have a similar figure. That means, now I say heat release per unit mass of products. That means q so much kilojoules per kilogram of product divided by as a function of mixture ratio. Well, it will be exactly similar and I get something like this. This corresponds to the stoichiometric mixture ratio.

Going one step further, I divide this q per unit kgs something like kilojoules per kilogram by the specific heat and therefore, now I can get the value of temperature verses mixture ratio. This is what I show in the next figure namely, I get a plot wherein the plot is like this. We must be able to differentiate between the total heat release and the heat release per unit mass and this heat release per unit mass when divided by specific heat will give me the value of the temperature which has a behavior something like this which I subsequently discuss.

There is a certain difference when I look at specific heats of substances which are formed in slightly fuel rich conditions. Under fuel rich conditions, you form substances which are little weaker CO instead of CO₂ and we found that diatomic species have higher value than monatomic species. Triatomic species have still different values. That means, as the atomic or the diatomic becomes triatomic, the specific heat increases and therefore, we find that specific heat is slightly lower in this region compared to the stoichiometric. Therefore, if I plot mixture ratio stoichiometric here, this is mixture ratio stoichiometric. You plotting mixture ratio here, I am plotting T_c over here. Instead of maximum temperature happening, it will occur at the fuel rich condition and I will get some shape like this.

Why did I say this? You find that when a substance is fuel rich, I form more of the smaller elements CO instead of CO₂ and therefore, CO has less specific heat compared to CO₂. Since, I am dividing by the value of specific heat by peak changes from stoichiometric to this, even though q_{per} this remains the same, that specific heats are lower as I go along this direction. Therefore, this peak changes by this particular $\left(\left(\right)\right)$. It is not very noticeable, but still we must remember this. The peak temperature occurs not at stoichiometric, but at slightly fuel rich condition and this is your oxidizer rich fuel.

Let us remember this slightly to the left. That means peak temperature occurs over here. Let us put the last point across. What is going to happen to the molecular mass of the reactance or molecular mass of the products? If mixture ratio is equal to stoichiometric, what is it we got? We got 8 CO₂ plus 10 H₂O. Therefore, the molecular mass is equal to 8 into 40, 4 plus 10 into 18 divided by 18. If it was more than stoichiometric, that is mixture ratio greater than stoichiometric when we had something like instead of 13 I had 15. What did I get? I got 8 into 44 plus 10 into water 18 plus 2 into 32 divided by 8 plus 18 plus 220.

I am looking at the mean molecular mass of the products. If I had something like mixture ratio which was less than mixture ratio stoichiometric, what is it I get? I still got water 10 into 18 and then, I found I had 4 of 30 2 4 of 40 4 carbon dioxide plus 4 of CO which was CO is 12 plus 16 28 divided by 4 plus 4 plus 118. What I am looking at the mean molecular mass of the products for stoichiometric for something mixture ratio greater than stoichiometric. That means this is oxygen rich. I am looking at mixture ratio less than stoichiometric which is fuel rich.

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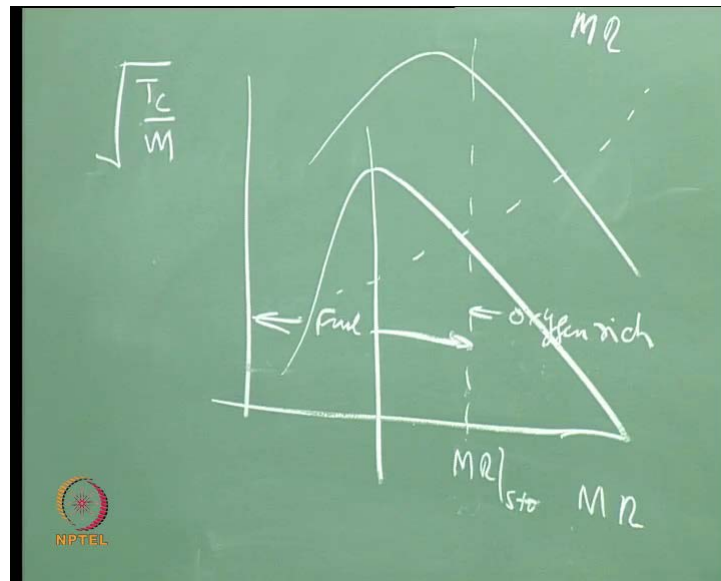
$$MR|_{\text{stoch}} = \frac{8 \times 44 + 10 \times 18}{18}$$
$$MR > MR|_{\text{stoch}} : \frac{8 \times 44 + 10 \times 18 + 2 \times 32}{20}$$
$$MR < MR|_{\text{stoch}} : \frac{10 \times 18 + 4 \times 44 + 4 \times 28}{18}$$

What are the values? Let us put down the values. I thought I had calculated. I am not very sure if I brought it. Yeah it should be here, may be this must be something like 290.5 11 O₂ is 26. Let us make an assessment rather than have the numbers clearly. What we find is for a stoichiometric I have this. When the mixture ratio is greater than stoichiometric, I am adding higher molecular mass. Therefore, the molecular mass is higher if I have mixture ratio less than stoichiometric. I am having I am adding substances which have lower value of molecular mass and rather I can plot this as the mixture ratio increases of the products mixture ratio. This is stoichiometric I get as the mixture ratio, the molecular mass increases.

What is it we were ultimately interested in? We were interested in the value of under root T_c by the molecular mass because c_{star} went as r t c. R t c is r not divided by molecular weight into t c and of course, gamma I am not considering. If I were to consider T_c by m verses mixture ratio, I find if I have stoichiometric mixture ratio stoichiometric, my temperature peak slightly in the fuel rich region. My molecular mass is increasing over here and therefore, the value of this will be in the fuel rich region. That means in my fuel rich region, I will have a higher value of c_{star} compared to stoichiometric and in the oxygen rich region.

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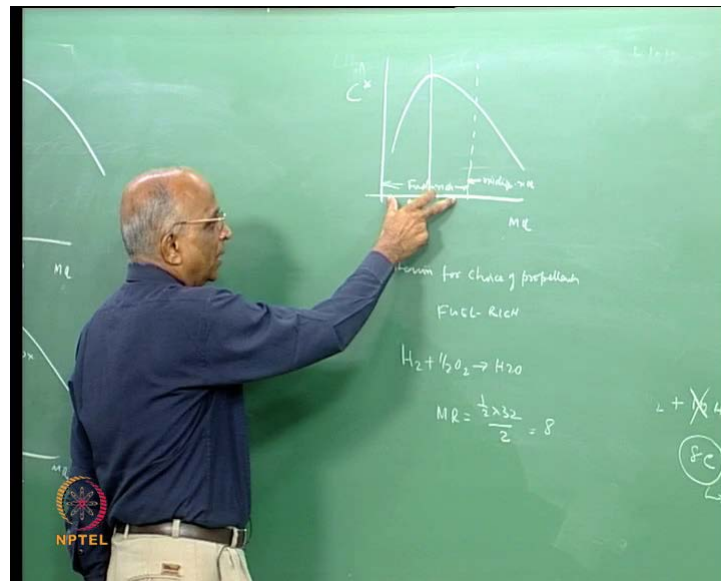


Let me re plot this figure because this is something which is important. The value of c^* as of plotted as a function of mixture ratio and this is mixture ratio stoichiometric. This is we are considering. Fuel rich oxidizer rich will be maximum in the fuel rich side.

Why it is higher in the fuel rich side? Because the molecular mass is smaller in the fuel rich side. We also find that the maximum temperature also occurs little bit on the fuel side and therefore, the net effect is I have higher performance in the fuel rich. Therefore, one of the criterion for choice of propellants is the propellant must be fuel rich. All propellants used are fuel rich propellants.

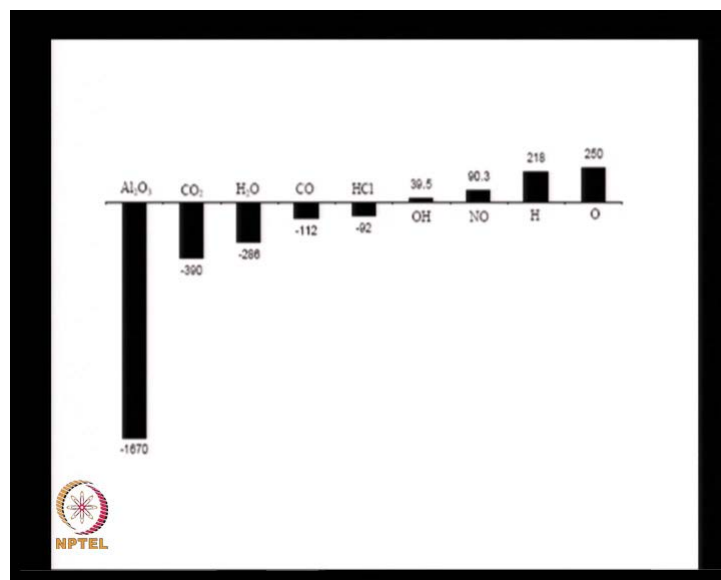
In other words, if I have stoichiometric reaction H_2 plus half O_2 giving me H_2O , what is it I am telling the mixture ratio in this case is going to be half into 32 divided by 2. That means we are talking of mixture ratio of 8 which is stoichiometric, but in practice what we use is mixture ratio between 5 and 6. The reason being yes, I get advantages of the lower molecular mass of the products and also to some extent, the saving from the specific heat.

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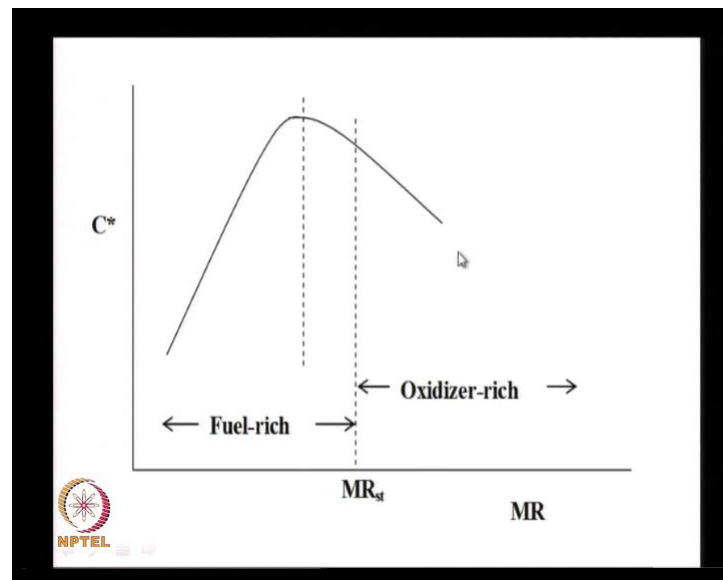
Therefore, what we have done in this class is we have told ourselves for the choice of propellants. It is better to have fuel rich propellants. That means mixture ratio less than mixture ratio stoichiometric.

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I will just go through the transparencies on this or the slides on this. Before I stop this class, maybe in the next class, we will take a look as you see the temperature is more slightly in the fuel rich side than in the oxidizer rich side. Therefore, c^* is higher in the fuel rich side compared to the oxidizer rich side.

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In the next class, we will take a small example and also we will try to take a look at what are the effects of dissociation, how to calculate with using equilibrium or chemical equilibrium. That is what we will do. Thank you.