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

We continue with chemical propellants in this class, namely the criterion for choice of propellants. What did we learn so far? We found that the propellants, which are chemicals must have low atomic mass, such that we have low molecular mass of products formed from combustion or chemical reaction. This was point 1. Point 2 we said was that the products could be dissociated. What do we mean when we 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 and the molecular mass will be smaller.

Third, we told ourselves from point of view of $\gamma$, it may be better to have more complex products of combustion. This complex product is against what we decided in point 2. Towards the end of last class, we also defined standard heats of formation and heat release from combustion. What did we say heat of formation is? We defined the standard heat of formation of a substance as the heat required to form one mole of the substance at the standard condition, the standard condition being one atmosphere pressure and say $25^{o}C$. The heat was required to form the substance at these standard conditions from the elements, which constitute the substance again at the standard condition. This is how we defined the heat of formation. This was the way we defined it for products, for chemicals or any substance.

The heat, which is released in a chemical reaction, we determined in the following way. If we have products being formed in a chemical reaction, the sum of the heat of formation of the products minus the sum of the heat of formation of the reactants with a minus sign gave the heat released. If the products consists of $n_1$ moles of substance 1, $n_2$ moles of the second substance and so on and each of these substances have the standard heat of formation, which is given by $\Delta H_f^0$ corresponding to the particular substance, we have the net value of heat of formation of the products as the summation of the moles

and the corresponding heats of formation. Well, this defined the heat of formation of the products.

Now, we subtract from it the summation of heat of formation of the reactants. If there is a decrease in the heat of formation, we said that energy is released in the combustion.

Let us be clear about this notation. If, we have for the reactants, $n_1$ mole of chemical 1, may be $n_2$ moles of chemical 2, etc., forming, let us say $n_1$ moles of product 1 plus $n_2$ moles of product 2 and so on. All what we say is for any specie i going from 1 to n for the reactants and 'i' going from 1 to n for the products and multiplying each for the corresponding mole with the corresponding standard heat of formation, we get the heat of combustion as the negative value of the difference.

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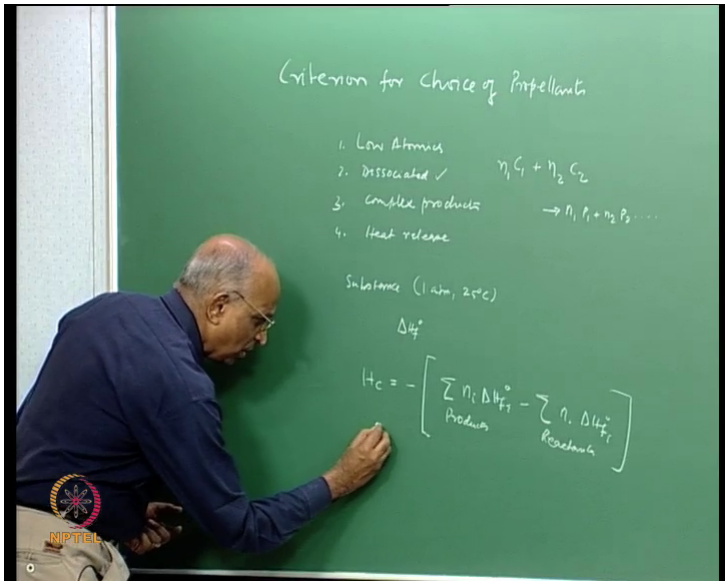


What is it that we want? We want this heat or which we also called as q to be as large as possible and for this we looked at heat of formation of different substances. We looked at heat of formation of let us say methane, ethane, propane, butane and all that up to kerosene, which we called as do-decane $C_{12}H_{26}$. We found that the heat of formation keeps increasing in the negative direction for this series of hydrocarbons. Therefore, we told that if the substance or the chemical is little more complex, may be the heat of formation is higher but negative. We also observed this trend in the example of $CO_2$ and CO. We found that the heat of formation of $CO_2$ was something like − 386 or −387 kJ/mole whereas for CO we found it was − 105.5 kJ/mole.

In fact, we used the reaction to find out the heat of formation of CO, heat of formation of $CO_2$ and as the product gets to be more complex in its molecular structure, the heat of formation was higher. Mind you it was negative or − 387 and − 105.5 kJ/mole. Therefore, we would like to know the conditions for the chemicals to produce maximum heat release.

What should be the choice of the substance with either large or small values of heats of formation, positive or negative? This is what we are trying to get it. Once we do this, we could be a little more wiser in the choice of propellants to be used for as rockets.

Let us get back to the slides. What I have shown here is the standard heat of formation for fuels such as methane −75 kJ/mole, ethane −85 kJ/mole, propane −104 kJ/mole, butane −125 kJ/mole. See it keeps on increasing and till we come to kerosene, it has increased and it is a much larger negative quantity equal to −293 kJ/mole. That means increasingly negative quantities as the molecule becomes longer.

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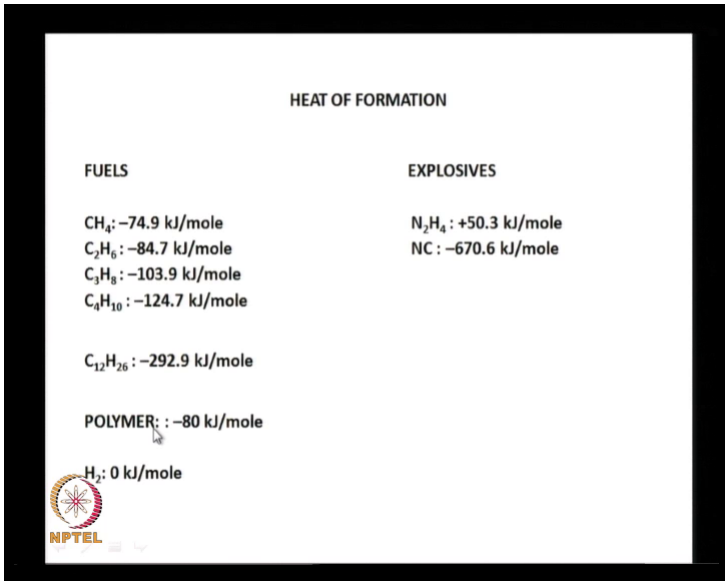


If we have a polymer; what is a polymer? Polymer is a slightly different animal, in the sense we are looking at something like a chain of C, H, O and perhaps N. The chain gets replicated a number of times. We find that the heat of formation of some of these polymers and we will look at polymers in some detail like poly butadiene later on when we deal with solid propellants. The polymer has heat of formation as shown in this slide of about − 80 kJ/mole.

When we talk of other fuels like hydrogen; hydrogen is an element and at the standard condition the heat of formation is zero. We conclude by saying that for different fuels, the negative values of heat of formation keeps increasing as the complexity of the substance increases. For a polymer, it is around −80 kJ/mole. For hydrogen, which is an element and again at the standard condition, it is 0 kJ/mole.

Now, we would like to include some more substances. In the last class, we said that there are some substances, which are known as explosives. We keep on reading about explosions. What is the difference between explosive and a fuel? When we have fuel and oxidizer already mixed together; mixed very well or if not premixed with the oxidizer and fuel are in the 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. In the last class, we dealt with nitroglycerine. When we say nitroglycerine is basically glycerin derived from propane. We make propane triol by hydrolyzing propane $C_3H_8$ and form $C_3H_5(OH)_3$. That is we take 3 of the 8 H atoms in propane and substitute it by OH. This is known as propane triol or glycerine. That means it is just an alcohol of propane. Now we substitute OH by a nitro radical $ONO_2$, we form the explosive. You get $C_3H_5(ONO_2)_3$ and this becomes nitro based on glycerine which is propane triol and this is known as nitroglycerine.

This has a heat of formation of 370 kJ/mole. How do you get it? You do an experiment by combining it or forming it with substances whose heats of formation are known. Why did I take this particular example of nitroglycerin. I want to know whether nitroglycerin can act as an explosive. It has oxygen, it has fuel, it can burn together to give me $CO_2$ plus $H_2O$ plus may be CO. Nitrogen, which is inert, is also present. However, if we look at the elements or atoms, which are there in nitroglycerin, we find it has 3 of carbon C, 5 of hydrogen H, 3 of nitrogen N, and 9 of oxygen O. That means it has 9 atoms of oxygen, 5 of hydrogen, 3 of carbon.

Now, if we want to oxidize the 3 atoms of carbon, we need something like 6 atoms of oxygen to form $CO_2$. We require two and half atoms of oxygen to form $H_2O$. Since we have 3 atoms of carbon, 5 atoms of hydrogen and 9 atoms of oxygen in one molecule of nitroglycerin, if we want all the carbon atoms to form carbon-dioxide, we need something like 6 O atoms. If I want to oxidize all the 5 atoms of hydrogen to form water,

we need two and half atoms of oxygen. Therefore, we require for complete oxidization 8½ O atoms; but I have 9 O atoms. Therefore, nitroglycerin could still act as an oxidizer even though it is an explosive. It has some oxygen left in it, which can still be used for oxidizing a fuel. Nitroglycerin we say is an oxidizing agent.

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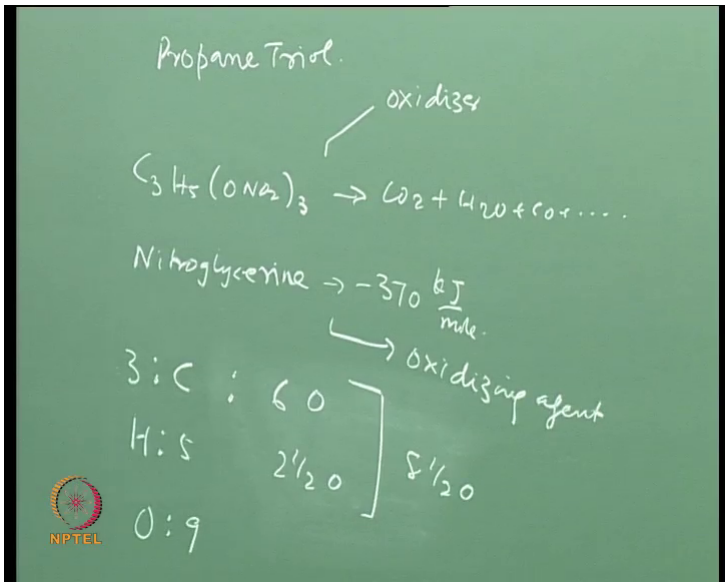


I will repeat this because it is something central to the choice of an oxidizer and a fuel in a propellant. Let us take a substance like nitric acid $HNO_3$. If we take nitric acid, we have one atom of hydrogen which requires half atom of oxygen for its oxidation. Therefore, we are still left with two and half atoms of oxygen. Therefore, nitric acid can be used as an oxidizer. That means it is an oxidizer even though it has fuel atom hydrogen in it.

If we 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 for ammonium perchlorate is $NH_4ClO_4$. We 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 has excess oxidizers in it and is an oxidizer. Similarly, if we have nitroglycerin, nitroglycerin can react by itself but can also provide oxygen. We can use it as a propellant directly, but I can also use it as an oxidizer in combination with some other fuel. In other words, we can use it as an oxidizer or else we can also use it in isolation as nitroglycerin itself.

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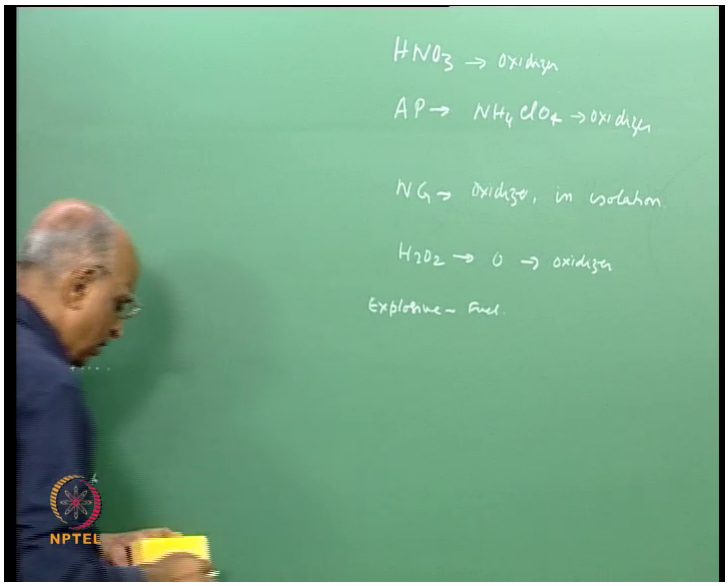


Similarly, if I take $H_2O_2$, which is hydrogen peroxide; we do not need both the O atoms in it to form water. We are left with one O after the fuel H is consumed and therefore $H_2O_2$ act as an oxidizer. Mind you $H_2O_2$ is an explosive just as nitroglycerin is an explosive. All these are all substances, even though they contain fuel is it, functions as an oxidizer.

Let us take one example of a fuel that is used with nitroglycerin. The example of this fuel also be an explosive, an explosive which can act as a fuel. The simplest one is may be like this wood, which is a cellulous material. The molecular formula for cellulose is $C_6H_{10}O_5$ and it consists of several such molecules to give its molecular formula as $[C_6H_{10}O_5]n$, where n is a large number.

Now, we can also write the above formula for cellulose as $[C_6H_5(OH)_5]_n$. Therefore, we say that it consists of n number of these molecules together. This is the equation to cellulous or formula for cellulose such as paper. Suppose, we nitrate it. That means I want to make nitrocellulose. We take some of the OH out and substitute it by $ONO_2$ and what we get is some part of the OH is left; but some are substituted by $ONO_2$. If of the 5 OH, x are removed and replaced by $ONO_2$, the chemical formula for nitrocellulose becomes $[C_6H_5(OH)_{5-x}(ONO_2)_x]_n$.

We now have the formula for nitrocellulose which is now C6H5, x of $ONO_2$ nitrate and 5-x of OH. Now, if we look at this, you know that the 6 carbon atoms will require 12 of

oxygen atoms to form $CO_2$. The 5 - x + 5 H atoms will require 5-x/2 atoms of oxygen to form water $H_2O$. The total requirement of O atoms is therefore 17 –x/2 of oxygen atoms. But the oxygen atoms, which is available, is only 3x plus 5 minus x, which is 5 plus 2x. The maximum value of x can only be 5. While the total requirement is 14½ , only 10 O atoms are available. Therefore, the availability of oxygen in nitrocellulose is much lower than the amount required for the oxidation of carbon and hydrogen present in nitro-cellulose.

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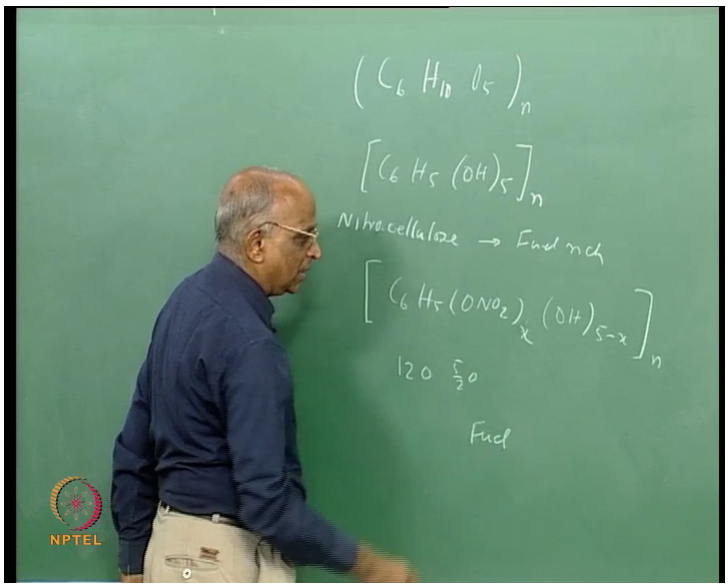


Therefore, in a sense the oxygen available within the molecule is much less than that required to oxidize the fuel component of carbon and hydrogen. Therefore, nitrocellulose is fuel - rich. It can dissociate by itself using the small amount of oxygen, but it cannot form completely oxidized species since carbon and hydrogen are more than the oxygen available in it. Therefore, it is also used as a fuel. We 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 its heat of formation, it has a large negative value, which is −670 kJ/mole.

We talked of hydrazine $N_2H_4$ in the previous lecture. Hydrazine which is again an explosive has the standard heat of formation of which is + 53 kilo joules per mole. We therefore observe, that explosives and other substances could act either as a fuel or an oxidizer depending on the relative amounts of oxidizer and fuel components in it. We

also see the heat of formation varies from something like a positive number of + 50 to a large negative value of − 670 kJ/mole.

We next take a look at the heat of formation of the oxidizers. An oxidizer could be oxygen. Oxygen is an element at standard condition. The heat of formation is zero. If we consider nitric acid, we just saw it is an oxidizer. Its heat of formation is −171 kJ/mole. If we remove the fuel component H from it and if we make into di nitrogen tetra oxide $N_2O_4$, which is a volatile liquid. The heat of formation is + 90.63 kilojoules per mole. We talked in terms of other oxidizers solid ammonium perchlorate whose chemical formula we said was $NH_4ClO_4$. $NH_4ClO_4$ has a heat of formation of −295 kJ/mole. If we instead of the perchlorate radical, we use the nitrate radical and get the oxidizer ammonium nitrate $NH_4NO_3$, the heat of formation is −365 kJ/mole.

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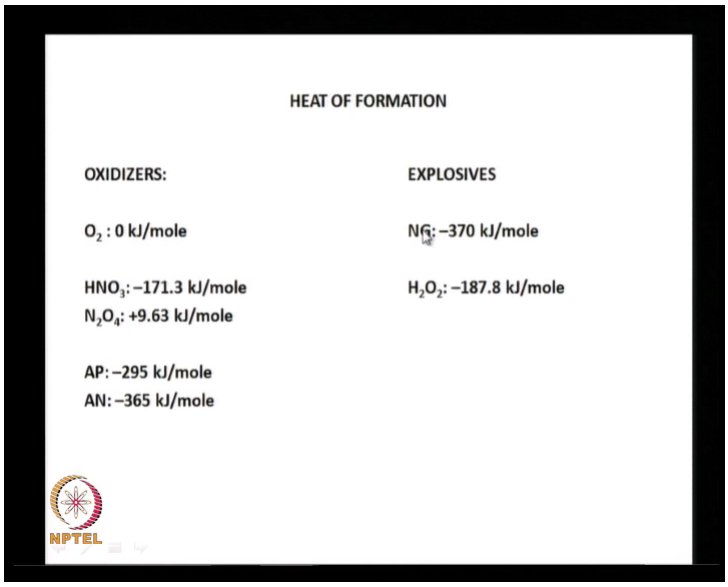


Therefore, you see the heat of formation widely varies for oxidizers also. In the case of nitroglycerin, it is −370 kJ/mole, for hydrogen peroxide it is −187 kJ/mole. Nitro nitroglycerin as a large negative value while $N_2O_4$ as a slight positive value. This is the variation in the heats of formation for oxidizers.

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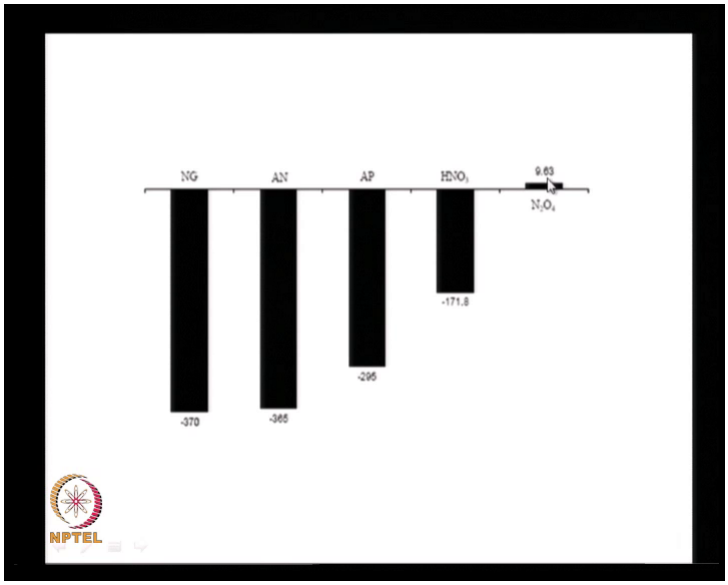
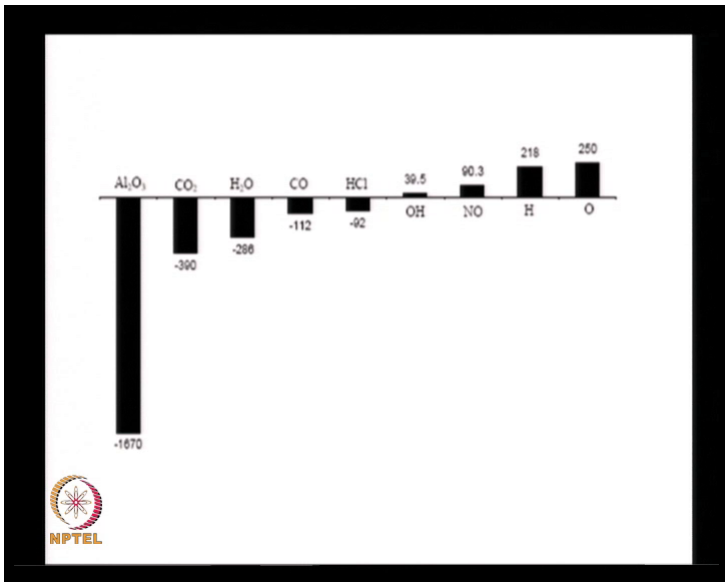



Similarly, for other chemical species such as the products from combustion or from a reaction; what are variations in the heats of formation? Well, carbon gets oxidized to $CO_2$ or CO. Hydrogen gets oxidized to $H_2O$. Therefore, the products are essentially $CO_2$, may be CO, may be $H_2O$ and so on. If we have aluminum in the metal, we could form aluminum oxide and these are some of the products, with which we are interested. And if you look at the heat of formation of some of these products which we worked out in the last class, it was something like −387 kJ/mole for $CO_2$, −110 kJ/mole for CO and −296 kJ/mole for water.



Why do we say water and not steam or vapor? Because we are looking at the standard condition of 25°C while the pressure is not that important for a liquid. Therefore, under standard condition, it is water. Therefore, the water has the standard heat of formation of −296 kJ/mole. H atoms dissociated was found to have a value of +217 kJ/mole. The heat of formation of OH was again high at +395 kJ/mole, but if we take aluminum oxide, it has an extremely large negative value of −1670 kJ/mole. Well, these are some values of heat of formation of fuels, oxidizers and products.

Now, we are interested in rocket propellants or chemical propellants, which will give as much heat as possible and therefore give a high value of temperatures. The negative of the difference between the net heats of formation of the products minus net heat of formation of the reactants is what gives us the value of the heat released (q). Therefore, we see that if the products could have individually negative values and if these negative values are large, we could have high value of heat release q.

Therefore, one of the requirements of chemicals, which can be used as propellants is that they must form products which should have large negative values of heat of formation. Mind you when we say products, by products we are not talking of chemicals. We are talking of may be $p_1$, $p_2$, $p_3$ or rather we are looking at $CO_2$, $H_2O$, CO., etc. The products must have large negative values of heat of formation. Is it ok?

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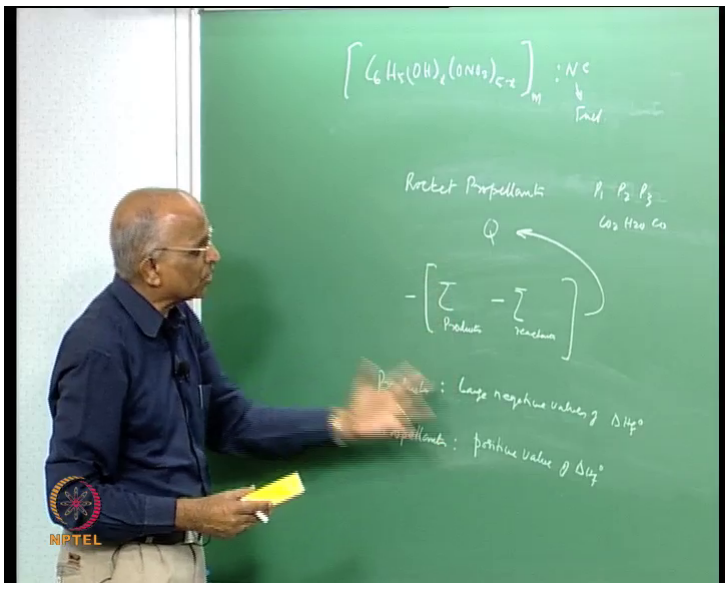

Similarly, if we talk in terms of the reactants; which are essentially the unreacted propellants, what should their heats of formation be? We have heat release is – {heat of formation of products – heat of reaction of reactants}. Therefore heat release goes as product of minus and minus which is positive. If the reactants would have positive value of heat of formation, it is better for us because we have a more positive number and greater heat release. Therefore, based on this logic, all what we say is if we have a propellant as a single chemical or a single substance or a combination of a fuel and oxidizer they must have small negative values of heats of formation or better to have large positive value of the heat of formation.

Why did we 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 heat to form the substance from its elements at the naturally occurring state and that it cannot remain so in the standard condition. Therefore, the general requirement is a small negative value, if possible instead of a large positive value, which is not possible.

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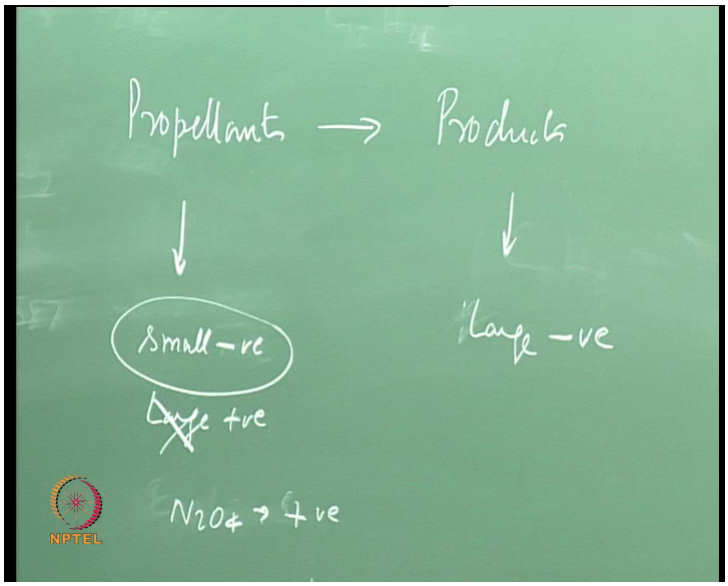


In general, some of the substances like $N_2O_4$ have small positive values of heat of formation; some of the explosives have positive values. We had considered these explosives earlier, but in general, most of the substances like kerosene have negative values. However, the desirable feature for a propellant is for large positive values of heats of formation though this is not possible in practices in view of such substances

being unstable. We sort of compromise with a small positive value or a small negative value. This tells us what is the choice of propellants from the heat of formation point of view.

If this part is clear, may be subsequent things are quite simple. Therefore, we tell that the choice of propellants for rockets should be such that they have positive value of heat of formation or small negative values and the products that they form should have large negative values of heat of formation.

We will do one or two problems towards the end of this class. It will become further clear to all of us. Let us consider a fuel like butane; unfortunately, butane is a gas and it is difficult to use, but let us take this example. We react it with oxygen as the oxidizer. Butane has the formula $C_4H_{10}$ plus oxygen $O_2$. The propellants we consider are therefore butane and oxygen. Let us say the propellants completely burn into carbon dioxide and water. Therefore we get 4 $CO_2$ plus 5 $H_2O$. Now, we want to balance this reaction. We require 8 plus 5 oxygen atoms giving 13 O atoms. Therefore, I get 13/2 of oxygen $O_2$.

So, we can write this reaction as 2 moles of $C_4 H_{10}$ plus 13 moles of $O_2$ give 8 moles of $CO_2$ plus 10 moles of $H_2O$. What is this reaction? In this reaction we form completely oxidized products of combustion. We cannot oxidize water any further. We cannot oxidize carbon dioxide further than this. Therefore, these are all completely oxidized products, completely oxidized or finished as it were. 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 word 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 we have for propellant butane as a fuel and oxygen as an oxidizer, is it possible that either more or less of oxygen than a stoichiometric reaction will give better value of C* through better values of temperature or smaller values of molecular mass of products. What will happen if instead of using 13 moles of oxygen, we were to have 15 moles of oxygen for every 2 moles of butane? In other words, we would like to consider proportion of fuel and oxidizer which is best suited for the propellant combination.

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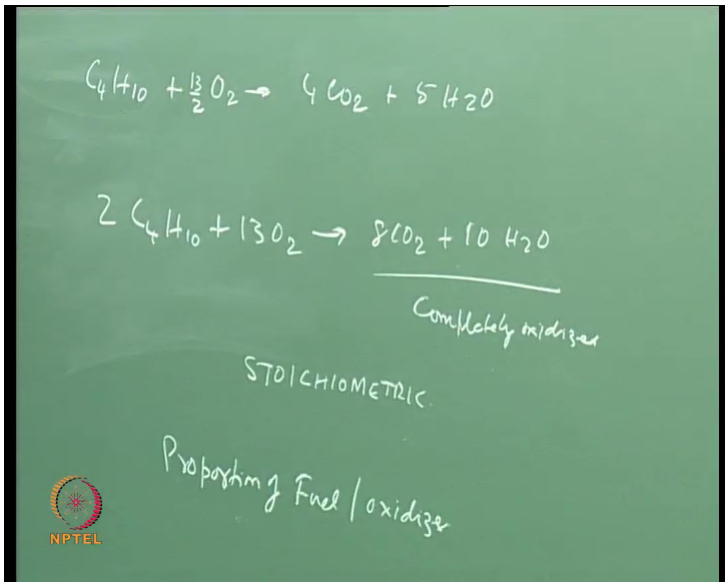


When we studied the subject of combustion, we talked in terms of equivalence ratio, which was defined as the fuel air ratio divided by fuel air ratio under stoichiometric conditions. In rocket propulsion, we use the word mixture ratio and mixture ratio is defined as of mass of oxidizer divided by mass of fuel in the propellant combination.

Let us illustrate it. If we want to find out what is the mixture ratio for this stoichiometric reaction between butane and oxygen. What is the mixture ratio? Mixture ratio for stoichiometric combustion of butane with oxygen is equal to mass of oxygen = 13×32. The amount of fuel is 2 × (12×4 which is 48 plus 10 which gives 58). The mass of oxidizer is 13×32. The mixture ratio is 13×32 ÷ 2×58. That is the mixture ratio for this reaction = 3.6. Therefore, if we use a fuel in the proportion of oxygen to fuel of 3.6:1, we get completely oxidized products of combustion.

How do you calculate the heat release in the reaction? All what we do is the heat release for this reaction is equal to – {(8 × −387, the value of the standard heat of formation of $CO_2$ + 10 × −286, he heat of formation of water) – (2 × −124.7, the heat of formation of butane + 13 × 0 the heat of formation of oxygen being zero since it is an element). The energy liberated in the reaction is therefore –{ (−8×387 −10×286) – (−2×124.7)}. This is the heat liberated in the reaction.

There is decrease in heat of formation as we go from reactants to products. we have to look at this from the net value of heat of formation of the products and the net value of

the heat of formation of the reactants. We find that there is a decrease and we have a minus sign. Therefore, we get 8×397 + 10×286 − 2 ×124.7 - so many kilojoules of energy, which is liberated. This is how we calculate the heat liberated in this stoichiometric reaction.

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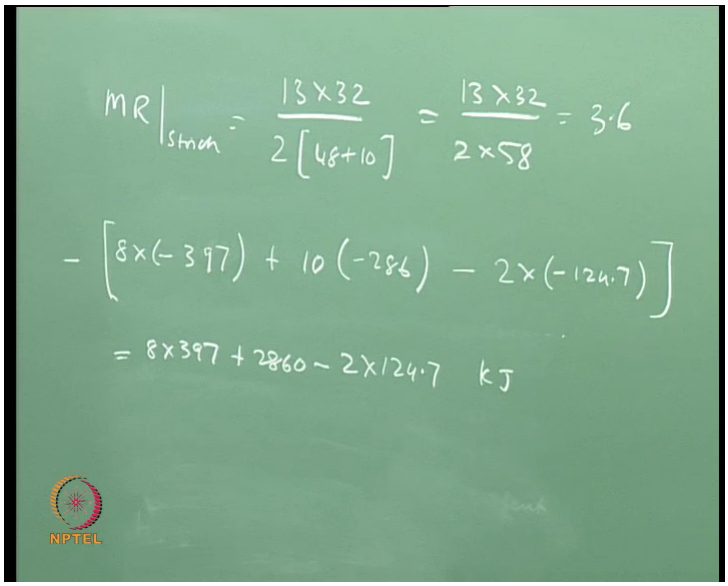


Instead of having stoichiometric composition, let us introduce extra oxygen into the reaction. We take the number of moles of oxygen to be 15 instead of 13 for the 2 moles of $C_4H_{10}$. Therefore 2 moles of $C_4H_{10}$ + 15 moles $O_2$ are the reactants. What is this reaction going to give as products? We have excess oxygen, therefore we still get 8 $CO_2$ + we get 10 $H_2O$ + we are left with 2 of oxygen $O_2$. This is because we have more oxygen than is required? The oxygen oxidizes the carbon and the hydrogen to form carbon dioxide and water and the balance $O_2$ is left in the products.

What is the mixture ratio for this reaction? It is equal to 15×32 mass of oxidizer mass ÷ 2×58 for mass of fuel. We just said the molecular mass of fuel is 48 plus 10 giving 58. The mixture ratio is 15×32/2×58 = 4.14. That means the mixture ratio has gone up from the stoichiometric value of 3.6 to a value of 4.14. Is the heat release in this reaction going to be different from the stoichiometric value. It will be same because oxygen here has zero heat of formation. Therefore, the heat of reaction is still at the same value.

Let us now consider the third case in which we have less of oxygen available than stoichiometric reaction. We take the same reaction of 2 moles of $C_4H_{10}$ plus instead of

giving 13 moles for stoichiometric reaction we have 11 moles of oxygen. That means we are starved for oxygen. If we are starved for oxygen, what is going to happen? You know I cannot get all $CO_2$, I cannot get 8 moles $CO_2$, I cannot get 10 moles of $H_2O$. The reason being we need 16 plus 10 atoms of O, i.e., 26 whereas we have only 22 of O. Therefore, it is not possible to get completely burnt products and balance the atoms on the left and right side of the reaction.

One of the ways we could do is to be able to find out what are the products that we will get? If we cannot get all carbon dioxide and all water, would we get CO, OH and other substances because there is inadequate oxygen to form carbon dioxide and water.

Now, how do we determine this? We cannot just like that determine the products of the reaction. We would have to do an analysis for the equilibrium composition of the products at a given pressure and temperature which means we have to use chemical thermodynamics to be able to determine this composition. However, this is involved and instead of analyzing the equilibrium of the products, there is an approximate or slightly easier method of doing this problem.

We say hydrogen is very reactive and therefore, all the 20 atoms of hydrogen, they search for oxygen and get converted into something like 10 $H_2O$, that is 20 of H pick up the 10 oxygen from the original 22 oxygen that we have. Since we have removed 10 from the 22 atoms of O, we are left with 12 O atoms. That means I have 20 atoms of hydrogen requiring 10 atoms of oxygen for forming 10 $H_2O$ because hydrogen is very reactive. But we find that we have 8 atoms of carbon and we cannot form 8 moles of $CO_2$ because this will require 16 atoms of oxygen. We have only 12 O atoms.

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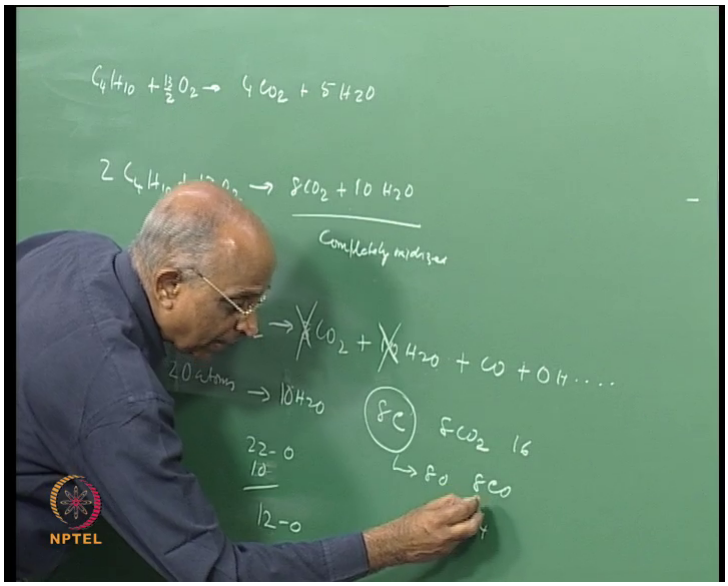


Since we have 8 atoms of carbon, let us first use the 8 of 12 atoms of O to form 8 CO. If, after doing this we are still left with O atoms, part of the CO will get oxidized to $CO_2$. We are left with 4 atoms of oxygen and what we do is use these 4 of oxygen to oxidize four of the eight CO to $CO_2$. Of the 8 CO, we remove 4 to form 4 $CO_2$ and therefore, the reaction will be: $2C_4H_{10} + 11\ O_2 = 10\ H_2O + 4\ CO_2 + 4\ CO$.

Let me repeat it. Some of you have done this method of calculating the products of fuel rich explosives in the explosion course. Since there is insufficient oxygen to form completely oxidized products of combustion, first the hydrogen attacks the oxygen because hydrogen is very reactive or rather the hydrogen removes part of the oxygen to form water. The balance of oxygen oxidizes the carbon to form carbon monoxide and if some oxygen is still left, the balance or the part of the carbon monoxide is converted to CO by the left over oxygen.

What is the heat release in this reaction? What is the mixture ratio of this particular reaction? Mixture ratio of this reaction is equal to $11 \times 32 \div 2 \times 58$ and this equals 3.03. What is the heat liberated in this reaction? The heat liberated in this reaction is – {(10 × the heat of formation of $H_2O$ + 4 × heat of formation of $CO_2$ + 4 × the heat of formation of CO) – (2 ×heat of formation of butane)}. Is it going to be higher or lower compared to stoichiometric reaction? It will be lower because CO has the heat of formation, which is −110 kilo joule per mole while CO2 has a higher negative value of − 397.

Therefore, you find that when a reaction is fuel rich or equivalently oxygen - lean, it is short of oxygen and the value of heat release comes down. If it is oxygen rich, then the heat release from the reaction is same as stoichiometric and this value is the maximum heat which is possible in a chemical reaction.

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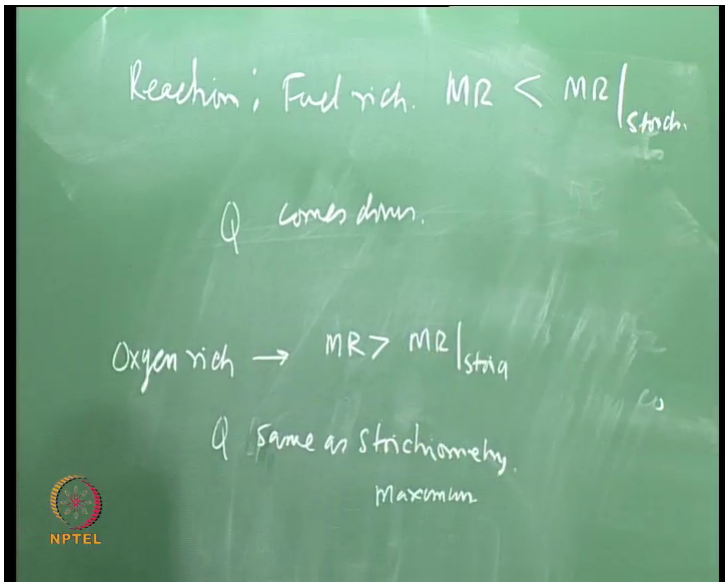


Let us ask one last question. Oxygen rich means the mixture ratio is greater than mixture ratio corresponding to the stoichiometric composition. Fuel rich means mixture ratio less than mixture ratio stoichiometric. If we plot the heat release from the chemical reaction, how will it look like? So, let us plot it. 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.

On the Y axis, we show the heat released in the reaction. On the X axis we show the mixture ratio. ? Suppose this is stoichiometric mixture ratio. I plot the heat release in the reaction as a function of mixture ratio. Based on our discussions, we find anything more than the stoichiometric mixture gives us 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, we want to convert the value of heat release 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 we want to convert it to temperature. We calculated in fact the heat of combustion or

the heat, which is liberated in the chemical reaction by looking at the products and their heats of formation. We said it must be less than the heat of formation of the reactants and the deficit is the heat, which is generated. Therefore, if we were to divide it by the summation of the mole and the corresponding specific heats, this will give me something like the temperature increase. It will give us the combustion temperature. That means specific heat × the number of moles of the products × the temperature increase is the heat release.

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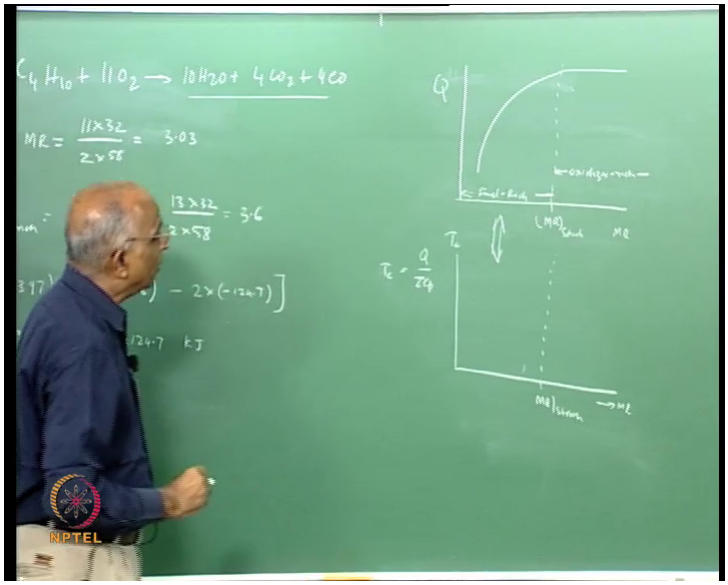


Therefore, the temperature of the combustion products in the combustion chamber Tc is equal to q / (Cp × the corresponding moles in the products). Again, we take the mixture ratio at stoichiometric condition and this is mixture ratio scale. Now, this is the temperature scale. Here, we have moles, which are coming in addition to the value of Cp. We need to be able to convert it because we have different number of moles. A direct comparison from this to the temperature may be a little difficult at the beginning. Therefore, what we could probably do is convert the heat release into heat release per mole.

Let us do this exercise. If you were to calculate it and we will go to the left side and plot the heat release q per unit mole of the products and this we note is similar q per unit mass. We plot this as a function of mixture ratio. Again this is the value of mixture ratio at stoichiometry. How will the curve for heat release translate into heat release per

mole? Let us do this exercise. Let us again go back into these equations and see for stoichiometric conditions. You have $C_4H_{10}$ plus 13 $O_2$. When it was oxygen rich, the number of moles increased and since the heat release q is same as it become more and more oxidizer rich. We plotted the heat release q so much kilojoules as a function of mixture ratio and the mixture ratio is at this point corresponds to mixture ratio 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.

We found when the oxygen content was more than what is required for stoichiometric mixture ratio, 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.

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

The X axis is mixture ratio and this point is the mixture ratios corresponding to stoichiometry. Now, what is happening as the oxidizer quantity increases; I am left with more of the products that is the number of moles of the product increases. Therefore, the value of heat release per mole begins to drop because the number of moles is increasing in the product after the point of the stoichiometric mixture ratio.

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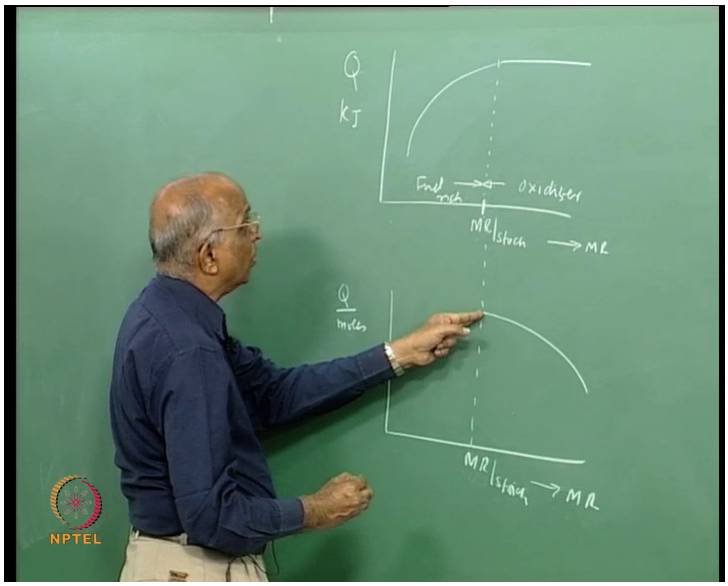


How about in the fuel – rich case? If the mixture is fuel rich, we are not able to form that much of moles now. Therefore, the number of moles of the product could decrease and therefore, this curve would become a little less drooping than what it was earlier. The peak value of heat release per unit mole is still at stoichiometric and the curve drops on either side in the fuel rich side and in the oxidizer rich side.

In other words, the amount of heat release per unit mole gives the maximum value at the stoichiometric mixture ratio and falls on either side of it. Instead of expressing heat release per unit mole, I can also have a similar figure for heat release per unit mass of products. That means q so much kilojoules per kilo gram of product plotted as a function of mixture ratio. Well, it will be exactly similar. The peak heat release 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 in kilo joules per kg Kelvin 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 temperature varies with mixture ratio as shown. 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 the mean value of specific heat will give me the value of the temperature which has a behavior something like this curve with the peak value at stoichiometric mixture ratio.

There is a subtle difference when we look at specific heats of substances, which are formed in the fuel rich conditions. Under fuel rich conditions, we are forming substances which are less oxidized like CO instead of $CO_2$. We had noted earlier that diatomic species have higher value than monatomic species. Triatomic species have still higher values of specific heat per mole. That means, as the diatomic species becomes triatomic at stoichiometric condition, the specific heat increases. Therefore, we find that specific heat is slightly lower in this fuel rich region compared to the stoichiometric. Therefore, if we plot mixture ratio stoichiometric here, this is the value of mixture ratio stoichiometric at which we obtained maximum heat release per mole. In the case of temperature Tc, considering the lowering of specific het in the fuel rich region and the flatness of the heat release curve at the stoichiometric mixture ratio here the maximum temperature Tc will get slightly shifted to the fuel rich condition and we will a some shape as shown.

In essence, when the propellants are fuel rich, we form more of the smaller elements CO instead of $CO_2$ and since CO has less specific heat compared to $CO_2$, we get a lower value of mean specific heat. Since we divide the heat release near the peak by the value of specific heat, even though the heat release remains about the same in the neighborhood of the stoichiometric mixture ratio, the value of peak temperature now shifts to the fuel-rich region. This may not very noticeable, but still we must remember the trends. The peak temperature occurs not at stoichiometric, but at slightly fuel rich conditions.

That means peak temperature occurs over here to the left of the stoichiometric mixture ratio. What is going to happen to the mean value of the molecular mass of the reactants and molecular mass of the products? If mixture ratio is equal to stoichiometric, what is the value of the mean molecular mass of the products that we got? We get 8 $CO_2$ + 10 $H_2O$. Therefore, the molecular mass is equal to $(8 \times 44 + 10 \times 18) \div (8 + 10)$.

If the mixture ratio was more than stoichiometric, we had the mean molecular mass of the products as $(8 \times 44 + 10 \times 18 + 2 \times 32) \div (8 + 10 + 2)$.

We are looking at the mean molecular mass of the products. If we had a mixture ratio which was less than mixture ratio stoichiometric, what is the value of the molecular mass? We get $( 10 \times 18 + 4 \times 44 + 4 \times 28) \div (10 + 4 + 4)$.

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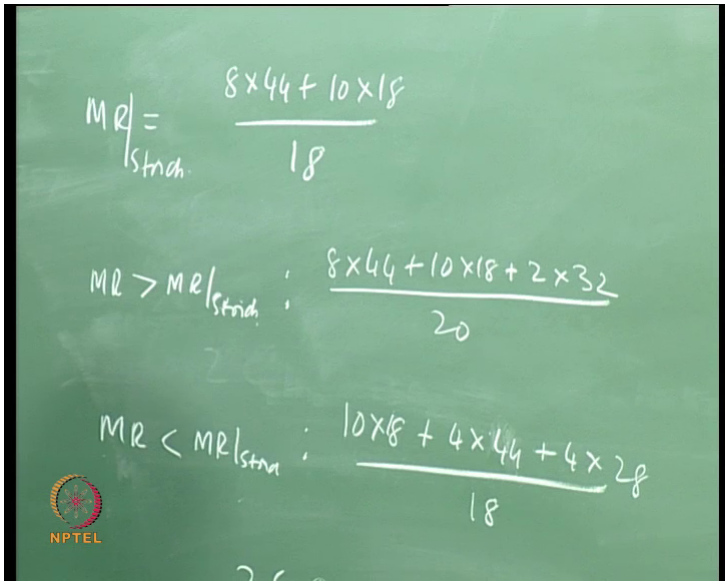


What are the values? Let us put down the values. It is 26 g per mole for stoichiometric mixture ratio. Let us make an assessment rather than have the numbers. What we find is for a stoichiometric we have this value of 26 g/mole. When the mixture ratio is greater than stoichiometric, we are adding substances of higher molecular mass. Therefore, the molecular mass is higher. If we have a mixture ratio less than stoichiometric, we are adding moles of substances, which have lower value of molecular mass at the expense of higher molecular mass and therefore the molecular mass of the products decrease. We can plot the molecular mass of the products as a function of the mixture ratio. We find that as mixture ratio increases the molecular mass also increase. The fuel rich mixture ratios give lower molecular mass for the combustion products as compared to stoichiometric mixture ratio.

What is it we were ultimately interested in? We were interested in the value of C* $=\sqrt{RTc} \div \Gamma$. The specific gas constant R is $R_0$ by molecular mass. If we were to consider Tc by molecular mass M verses mixture ratio, we find that the temperature peaks in the slightly fuel rich region. The molecular mass increases as the mixture ratio becomes increasingly fuel rich; that is as the mixture ratio keeps decreasing. That means we will have a higher value of C* in the fuel rich region compared to stoichiometric and oxygen rich mixture ratios.

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Let us re-plot this figure of C* versus Mixture ratios. The peak value of C* occurs for mixture ratios less than stoichiometric in the fuel rich side.

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

In other words, if we have stoichiometric reaction of fuel $H_2$ plus oxidizer $O_2$ giving me $H_2O$, what is the stoichiometric mixture ratio? The stoichiometric reaction is 1 mole of $H_2$ reacting with half mole of $O_2$. The mixture ratio in this case is $½ \times 32 \div 2 = 8$. That means we are talking of mixture ratio of 8, which is stoichiometric. In practice what we use is mixture ratio between 5 and 6. The reason being we get advantages of the lower molecular mass of the products and also to some extent, higher temperatures at the mixture ratios less than stoichiometric, the dominant factor however, being the molecular mass.

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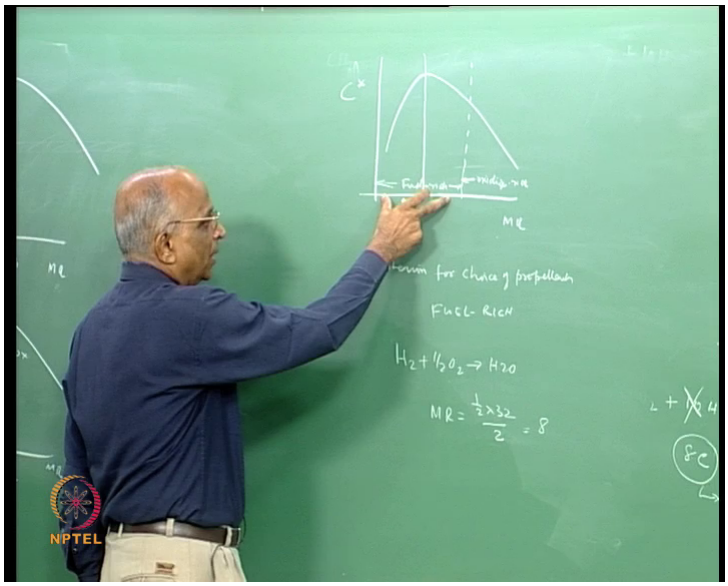


Therefore, we find that it is better to have fuel rich propellants. That means mixture ratio less than mixture ratio stoichiometric.

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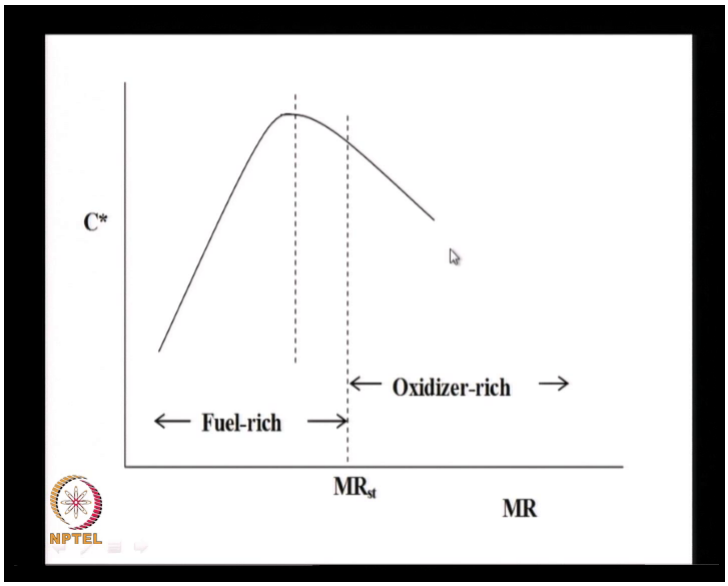


In the next class, we will take a small example and also analyze the performance of rockets.