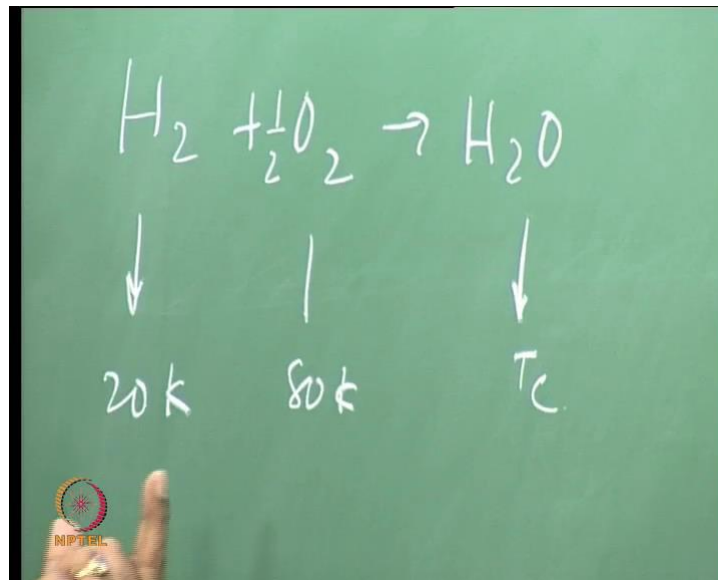


Rocket Propulsion
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Module 01
Lecture 17
Performance Prediction and Analysis

Good morning. In the class today, we will extend what we did in the last class and look at the reaction of hydrogen and oxygen to form water. When we use hydrogen as a propellant, it is not used a gas at the standard conditions but as a very low temperature liquid. Similarly, oxygen is used as a liquid at low temperature.

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We use hydrogen at a temperature about 20 K, oxygen at let us say 80 K; our interest is to determine what will be the temperature of water which is formed. Mind you, as per these reaction: $\text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O}$. The question is to estimate the temperature when the initial condition of hydrogen and oxygen is not standard, but drastically different from the standard conditions.

However, before we do this, let us again be very clear of we did in the last class. We had said that the value of C^* is a maximum when the mixture ratio is less than mixture ratio corresponding to stoichiometry. That means in the region of fuel rich conditions, we have higher value of c star compared in the oxidizer rich and stoichiometric condition.

It is very rare that rockets are operated under oxidizer rich condition because you have higher molecular mass and you do not get the advantage of temperature either. Therefore, we normally choose compositions, which are fuel rich.

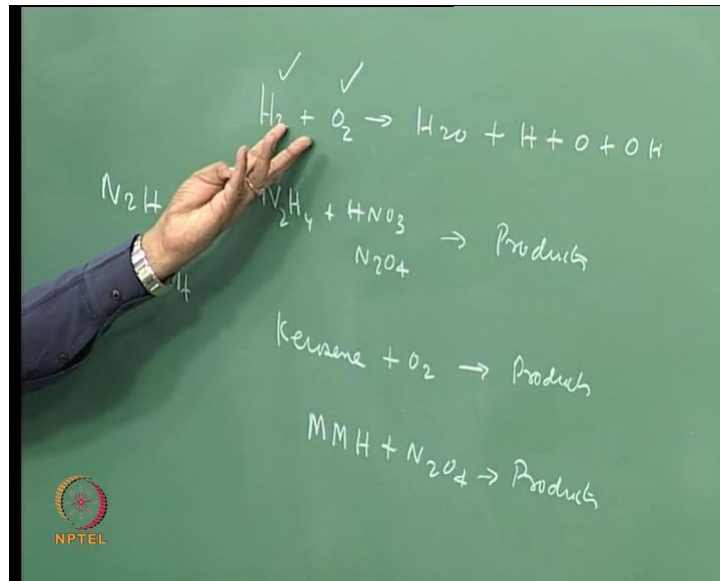
Since we studied what are the conditions required in the choice of propellants, let us just put down some five or six propellants which we can say are viable propellants. One is let us say hydrogen and oxygen to give me H_2O as products; but we want to operate it under fuel rich conditions. Therefore, I will get something like H_2O plus H plus OH and so on because we do not have sufficient oxidizer to form water and further at the high temperatures water formed could dissociate.

Therefore, we say the hydrogen with oxygen could be one of the propellants and let us do a small problem under stoichiometric conditions and then extend it to fuel rich condition. The other propellant we said could be hydrazine N_2H_4 . We said oxidizer could be nitric acid HNO_3 or better still compared to nitric acid, we said N_2O_4 , which has a small positive value of the heat of formation. Therefore, hydrazine and N_2O_4 is a good combination and this would again give some products. Why not we think in terms of kerosene? Kerosene had a large negative value of the heat of formation, but not too very large. It has a heat of formation of about -200 kJ/mole and you could react it with oxygen to form products. Again I choose fuel rich condition and this could be a good propellant.

You find that substances like nitric acid may be N_2O_4 are widely used as oxidizers. Hydrazine is also used and we will see the advantages of using hydrazine with nitric acid and N_2O_4 . Instead of hydrazine N_2H_4 , we could remove one of the hydrogen atoms giving N_2H_3 and substitute it with the methyl radical and it becomes one or mono methyl hydrazine. It is known as mono methyl hydrazine (MMH), The combination of mono methyl hydrazine and N_2O_4 is a very popular propellant combination. Mind you, it is also used as fuel rich and not oxidizer rich or stoichiometric. We can keep on adding different fuels and oxidizers to form propellant combinations.

When the fuel and oxidizer are in gaseous state at ambient temperatures like hydrogen and oxygen, we could liquefy them and use them as a liquid propellants.

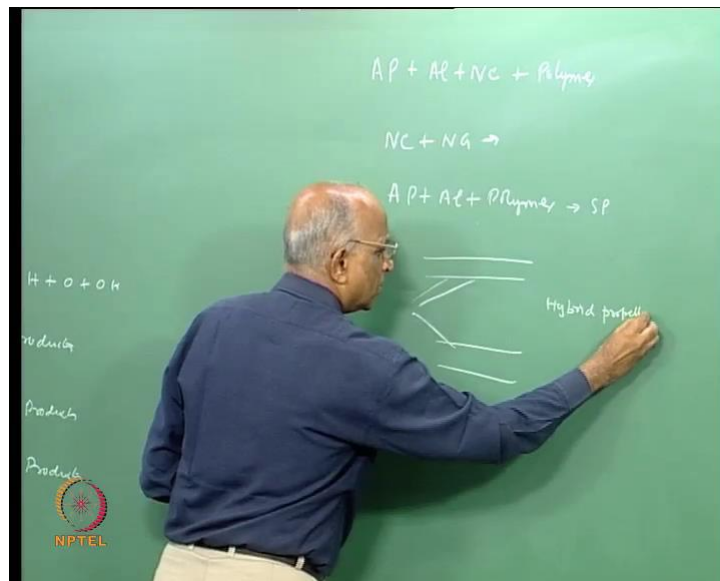
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The above fuels and oxidizers were in liquid phase; we could also have solid fuels and solid oxidizers including solid explosives. What could be the solid fuel and a solid oxidizer? We had ammonium perchlorate, which was an oxidizer plus a polymeric fuel or an aluminum metal. We also mentioned in the last class, about nitrocellulose could be used as a fuel or else polymer could be used as a fuel. We normally do not combine the solid oxidizer ammonium perchlorate with aluminum and nitrocellulose but rather we combine nitrocellulose and nitroglycerin to give a solid propellant. We also combine ammonium perchlorate plus aluminum plus polymer to form a good solid propellant.

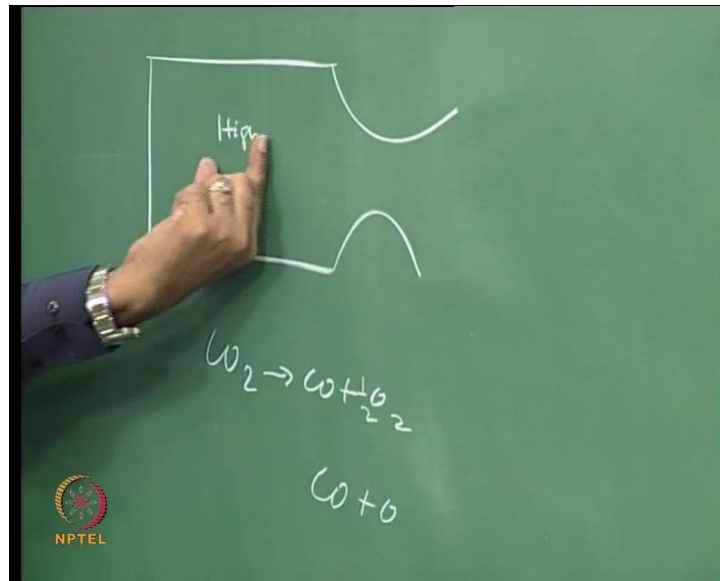
Well, the selection of the number of chemicals or chemical substances in liquid and solid forms to give liquid and solid propellants is somewhat limited. We cannot have an infinite number of propellants because we need a high value of C^* . In the case of solid propellants, we could have used either nitrocellulose or nitroglycerine singly by itself in which case we say they are single base propellants. When used in combination i.e., nitrocellulose and nitroglycerine together, they become a double base propellant. There are two bases. Each one could be a propellant, but a combination could also be a propellant. We could also have a composite mixture of ammonium perchlorate aluminum and polymer to give me something like a solid propellant.

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We have talked in terms of liquid and solid propellants. We could also think having a solid fuel with a liquid oxidizer and vice versa in which case we are considering hybrid propellants. We take the polymer and cast it over as a solid. We allow the acid (liquid oxidizer) to fall on it. The combination of liquid and solid and this gives us, what we call as a hybrid propellant. We make sure that the rate of reaction in the fuel rich region is such that we get a high value of performance parameter C^* . This is all about the different types of propellants but I think we have to get into some more depth of how the initial conditions of temperature and pressure influence the C^* ; how do you get the temperature of the combustion products?

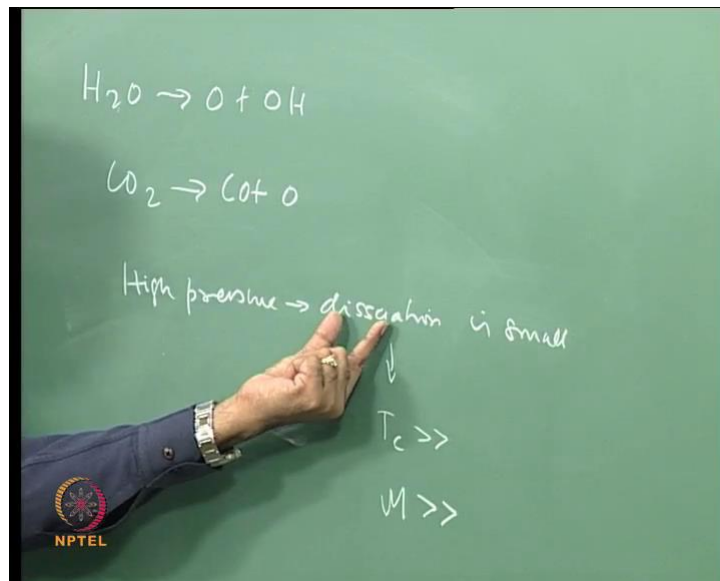
We have a chamber in which chemical reactions are taking place. Supposing we have high pressures; very high pressure in the combustion chamber. If we have high pressure, the amount of dissociation that takes place would be less. What do we mean by dissociation. The CO_2 formed in the products becoming CO plus O or rather let us say into $CO + \frac{1}{2} O_2$ or $C + O_2$. You know if we have a high pressure environment, we cannot increase the number of molecules that easily and to make gases dissociate or breakup at high pressures is more difficult than at low pressures. This is because pressure tries to reduce the volume and does not favor an increase in the number of molecules. We have to increase the volume to accommodate the increasing number of molecules for which we essentially need low pressures. (Refer Slide Time: 06:10)



But we have still not considered the effect of pressure. It must come through dissociation of the products. Let us see some results on what will be the effect of dissociation. All what we say is a dissociation reaction is one in which we are breaking up the more complex molecules into simpler ones. What is breaking up? May be water breaks up into O plus OH. Why does it break up? The temperature is so high and it has so much of energy in it that it tries to break up.

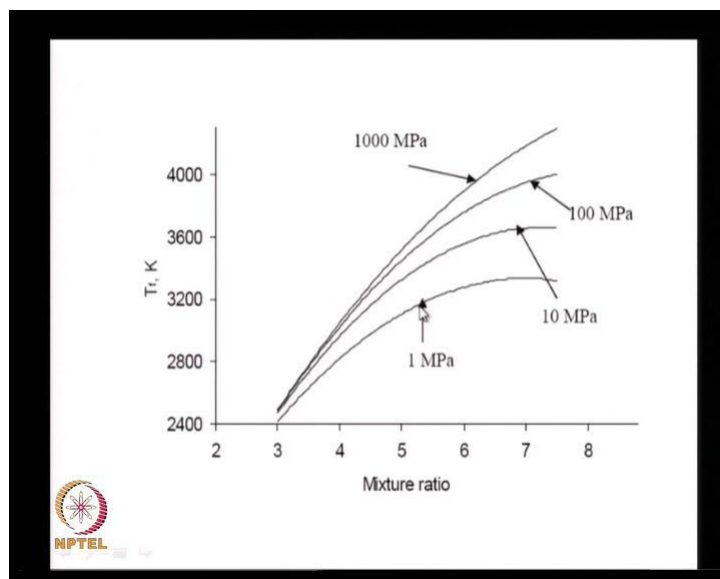
Similarly, I have CO_2 . It is trying to break up into $\text{C} + \text{CO} + \text{O}$. Let us say you know when this breakup will be possible. At extremely high temperatures, at the temperatures encountered. However, if we have a high chamber pressure, the pressure will try to prevent the increase in the number of molecules. The amount of dissociation will be much less at high pressure than at low pressure. At low pressures the resistance to an increase is less and the products can dissociate much more easily.

At high pressure, this is not possible and therefore, I find that high pressure, the dissociation is small. If the dissociation is small at high pressures, well energy is not lost. In this case, since dissociation is less, the temperature T_c will be higher. But since dissociation is small, the molecular mass will also be large. However, the effect of temperature T_c will much be more dominant than the increase in the molecular mass and therefore the increase of pressure could still have a favorable effect on C^* . (Refer Slide Time: 07:22)



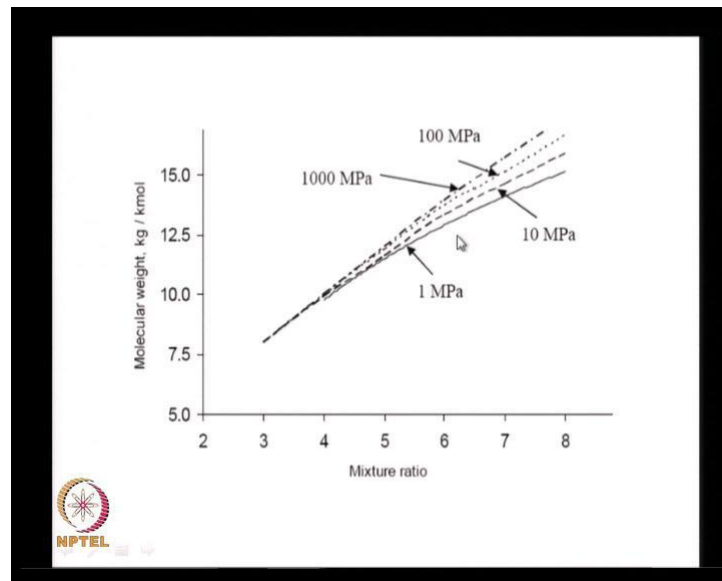
Let us take a look at typical results in a rocket using hydrogen and oxygen. We are still have to do the theory part of it; nevertheless let us examine some results. The temperature of the products of combustion as a function of mixture ratio for a fuel rich hydrogen oxygen mixture at a pressure of one 1 MPa, 10 MPa, 100 MPa and 1000 MPa is plotted in the following slide as a function of mixture ratio.

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You find that at a given mixture ratio, as the pressure increases, the temperature increases because at high pressure, the amount of dissociation is less. More completely oxidized products of combustion having more negative heats of formation are formed.

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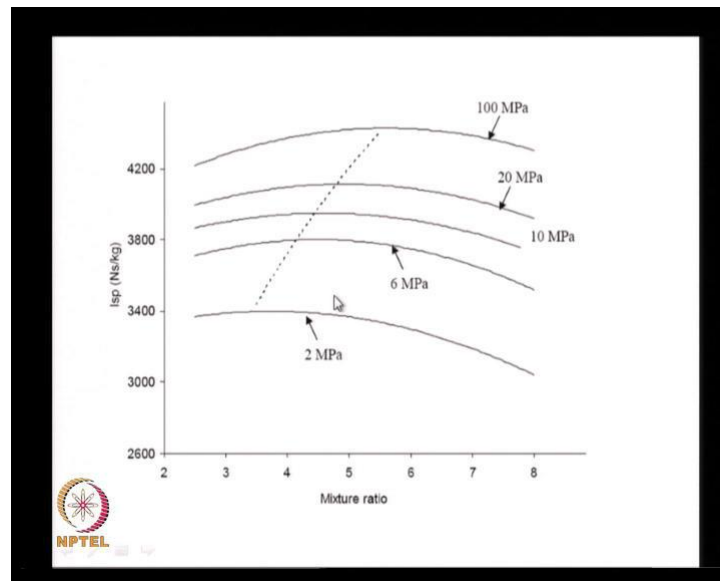


You also find that the molecular mass of gases increases with mixture ratio as determined by us earlier. But we also find that as the pressure increases, the molecular mass increases. Why is that? At higher pressures we have less dissociated gases and dissociated gases have a low molecular mass. Is it clear?

Let us go to the next one. If now I say the value of gamma, we said gamma is higher for the mono atomic species, 1.67 for helium, for very complicated CCl_4 it is about 1.13. Therefore, you find that as the chamber pressure increases, the dissociation is less and therefore, the gamma value is smaller. With increase of mixture ratio we have already seen the variation of gamma with mixture ratio. If it is more oxidizer rich, we have heavier products, which are formed and therefore, the gamma is decreasing, but more importantly now we are considering the effect of pressure. As pressure increases, the value of gamma decreases.

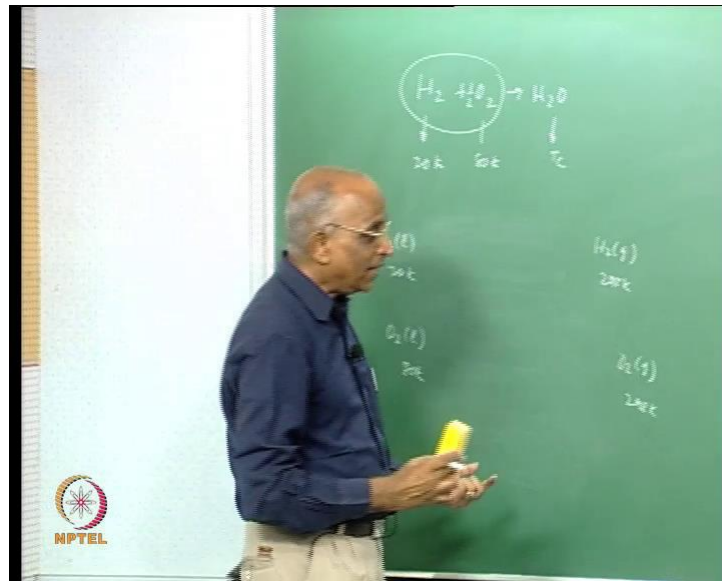
Why does this happen? Because I have more complex molecules at higher pressures, dissociation is less. If we put all the factors together, we find the C^* or equivalently the I_{sp} increases. This is because the I_{sp} is equal to C^* into the nozzle performance. We also find that as pressure increases, the optimum value of the mixture ratio for which I get the maximum value of C^* keeps changing.

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Therefore, there it is not only just the mixture ratio alone, which decides the maximum value of specific impulse, but the pressure is important because pressure influences the amount of dissociation. This is for hydrogen oxygen propellant combination. Therefore, we have to take a look at dissociation and these are results for which we are not yet equipped to do the analysis, but we will be doing it. Therefore with this background into what happens when we have a chemical reaction at different values of pressures for the reaction of hydrogen and oxygen, let us find out the temperature of the combustion products.

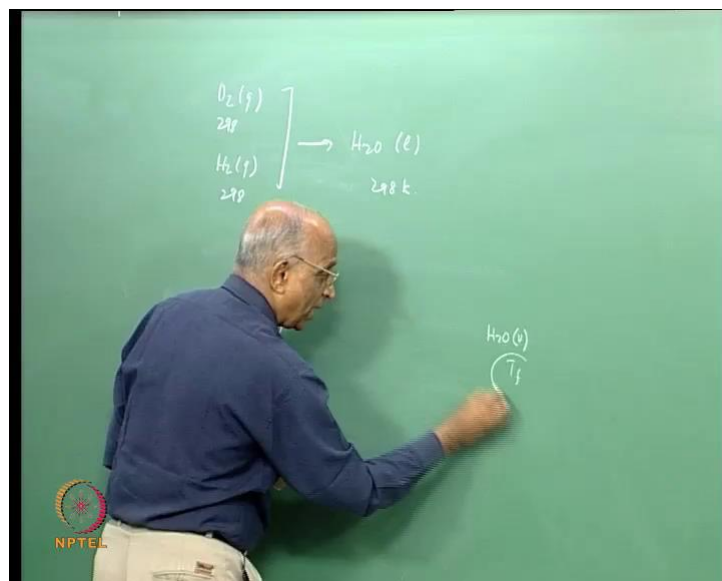
How do we do this problem? We would first like to understand what is the heat generated in this reaction. Hydrogen and oxygen are not at the standard state of 298 Kelvin, but hydrogen is a liquid. we use it as a liquid at 20 Kelvin; we use oxygen as a liquid at 80 Kelvin instead of a gas at 298 Kelvin. Therefore, we have to first convert these two substances, which are at a reduced temperature to 298 Kelvin. In other words, I would like to take hydrogen, which is a liquid at 20 Kelvin, convert it ultimately to hydrogen as a gas at 298 Kelvin before we can use the standard heat of formation. (Refer Slide Time: 11:54)



Similarly, I have to heat liquid oxygen, which at 80 Kelvin, convert it into oxygen gas at 298 Kelvin. Once I have converted this, then the standard heat of formations can be used. Thereafter, we can take this liquid oxygen, which is at 298 Kelvin and gaseous hydrogen, which is at 298 Kelvin. And combine them to form water H_2O , which is a liquid at 298 Kelvin.

Heat is generated in the reaction between hydrogen and oxygen. This heat converts the water to H_2O vapor at high temperature T_f or T_c and it is this temperature that we require to determine.

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No heat is lost to the ambient nor is heat gained from it. Therefore, the process is adiabatic. We call the temperature, if the process is adiabatic; as adiabatic flame temperature. Therefore, we would like to find out the adiabatic flame temperature of the products of combustion when the reactants are not at the standard state, but in a state of liquid at low temperatures.

Therefore, what is it we have to do? I have to first take this hydrogen which is a liquid, take it to its boiling point at which it is still a liquid and boiling point of hydrogen is about 22 K. That means this is sensible heat wherein we still have the liquid phase and then once it has reached the boiling point at 22 K, we supply the latent heat or heat of the vaporization and convert it to H₂ vapor again at the boiling temperature itself. This is a constant temperature process taking place at the boiling temperature T_b, which we said we said is 22K at the stated pressure. Once it has become vapor, again I provide sensible heat and increase the temperature from 222 to 298 K.

Therefore, heating of the liquid, conversion of the liquid to vapor and heating of the vapor to the standard condition is what is required here. Similarly, for oxygen: oxygen is a liquid till the temperature of boiling, temperature of oxygen is around 90 Kelvin and then we convert it using latent heat into oxygen vapor. Thereafter we increase the vapor temperature to the standard at 298 K.

What is the process with respect to the products? We have H₂O as a liquid which is formed at 298 K. Mind you, 298 K is 25°C. We have to heat it as water again till the boiling temperature of water. Let us assume the boiling temperature to be 100°C and at 100°C what do we have to do? We have vaporization, that is heat has to be supplied for the latent heat to form water vapor. Now, this conversion is again at 100°C and then we convert the 100°C vapor to the final adiabatic temperature T_f.

Therefore, the heat, which is generated by the reaction at the standard state, should be able to supply heat for the conversion of liquid hydrogen and liquid oxygen to a vapor at the standard state plus taking the water to this particular temperature. Therefore, let us write the equations. I think this energy equation is important because we do not ever use propellants always at 25°C. Sometimes in a cold condition, like for instance, whenever we use N₂O₄, we chill the N₂O₄ and use it. Otherwise, it tends to vaporize.

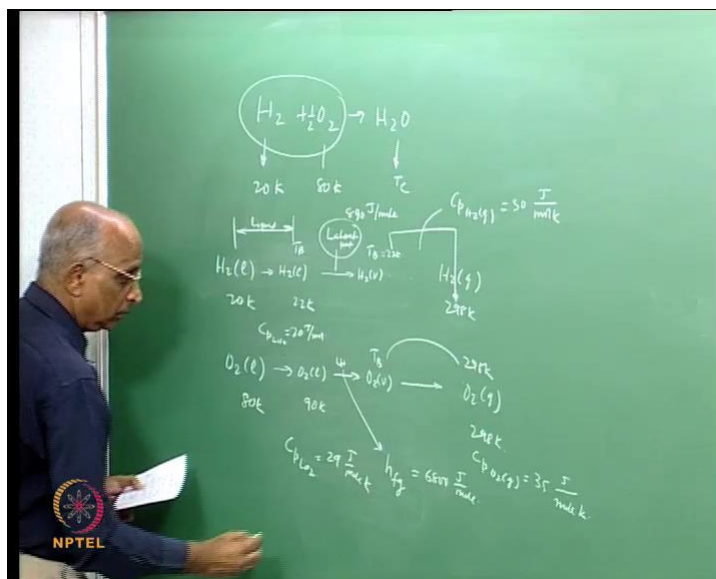
So, can we start with the energy balance relation? Is it clear? All what we did while estimating the heat release is that the propellants were originally at the standard state and the products were also formed at the standard state and we calculated the heat which is

generated at the standard state. We had for the heat release from the standard heat of formation of water as $\Delta H_f^0 = -286$ kJ/mole. The standard heat of formation of the reactants hydrogen and oxygen was 0 giving the decrease in the heat of formation of products as $-(-286 + 0) = 286$ kJ/mole of water formed. Therefore, the heat generated is equal to 286 kJ in this reaction.

We never bothered about the heat of this reaction, which goes into conversion of the reactants to standard state and the products to the final temperature. Let us put this data clearly. We have hydrogen as a liquid at 20 K, the boiling temperature is 22 K and we need heat for this change. The specific heat of the liquid hydrogen is equal to 20 joule per mole Kelvin. The latent heat of conversion of liquid hydrogen to hydrogen vapor at the constant temperature of 22 Kelvin is equal to 890 joule per mole. We prefer to use mole as the unit of the quantity of a substance because it tends to be simpler because chemical rate equations are written in terms of moles.

Similarly, for oxygen the specific heat of liquid oxygen is equal to 29 joule per mole. The latent heat that is equal to 6800 joule per mole compared to 890 J for hydrogen. We need two more things. We need the specific heat of oxygen as it increases in temperature as a vapor. That means we are looking at specific heat of hydrogen as a gas and similarly, specific heat of oxygen as a gas.

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The specific heat of hydrogen as a gas is equal to 30 Joule per mole Kelvin and the specific heat of oxygen is equal to 35 J/(mole K). We should have had the word Kelvin here. Whenever we have specific heat, we are talking per unit temperature change and similarly, when we talk in terms of water, we have specific heat of water and steam.

The specific heat of water is equal to $90 \text{ J}/(\text{mole K})$, the latent heat h_{fg} for water is equal to $35 \text{ kJ}/\text{mole}$. Again we check these numbers. Yes, $35000 \text{ Joule per mole}$ and specific heat of vapor is equal to $58 \text{ J}/(\text{mole K})$.

We have the heat determined under standard conditions; We were able to write if H_2 is at 298 Kelvin and it reacts with half of oxygen, again at 298 Kelvin , we form water one mole of water at 298 Kelvin . In this case, the heat of formation of water is equal to minus $286 \text{ kilo joules per mole}$ and we got the energy release as $286000 \text{ joules of energy per mole of water formed}$.

This heat raises the state of liquid hydrogen and liquid oxygen to the standard state and raises the temperature of water to the final temperature. Let us put this in a better form. The heat given to one mole of liquid hydrogen starts with 20 K , goes to boiling point at 22 Kelvin . This corresponds to C_p of liquid hydrogen into 2. Plus we have h_{fg} corresponding to the hydrogen going from liquid to vapor plus we have the temperature rising between 22 and 298 K . The value of C_p corresponding to gaseous hydrogen in joules per mole K is used here. We repeat the same for oxygen. I have from 80 Kelvin to the value at 90 which is the boiling temperature is equal to C_p corresponding to liquid oxygen plus h_{fg} corresponding to oxygen at 80 Kelvin plus the sensible heat in going from 80 to 298 K with the corresponding to C_p of oxygen gas.

Whatever we have written here through arrows is expressed in the above. We have assumed C_p to be constant in this particular region and whenever we say C_p is a constant, we assume it something like a perfect substance.

Let me not do this exercise by putting the actual numbers. I will just call it as h_1 . What is h_1 ; so many joules, corresponding to the sensible and latent heats. Now, I want to know the value for water. What happens to water? Again, one mole of water is formed. I think we forgot something. See this is per mole, per mole, per mole is when I have one mole of oxygen. It is half mole here. We have half mole because h_{fg} was per mole. Therefore, h_1 should contain half mole of oxygen and one mole of hydrogen over here. (Refer Slide Time: 21:42)

$$\int_{20}^{22} C_{p, \text{H}_2} dT + h_{fg} |_{\text{H}_2(\text{liq})} + \int_{22}^{298} C_{p, \text{H}_2(\text{g})} dT$$

$$+ \frac{1}{2} \int_{80}^{90} C_{p, \text{O}_2} dT + \frac{1}{2} h_{fg} |_{\text{O}_2(\text{liq})} + \frac{1}{2} \int_{90}^{298} C_{p, \text{O}_2(\text{g})} dT = H_1(\text{J})$$

$$C_p = \frac{\text{J}}{\text{mole} \cdot \text{K}} \quad h_{fg} = \frac{\text{J}}{\text{mole}}$$

Let us remember that we defined C_p as J/(mole K). We define the latent heat of vaporization as J/mole. If you are going to use the mass units and specific heats as joule per gram Kelvin or joule per kilo gram Kelvin, better to convert the mole into gram or mole to mass and then use this relation. However, working with moles is very much simpler.

Now, for water formed as combustion products; we again take one mole of water is formed at 298 K. Therefore, you have to heat water from 25°C to the boiling temperature of water assumed as 100°C. If the pressure is higher, the boiling temperature will go up. C_p for water as a liquid which we know $\times (100 - 25)$ plus h_{fg} for water which is given in J/mole + we have the sensible heat from 100°C to the value of final temperature T_f , which the adiabatic flame temperature. Here C_p is the specific heat of the vapor. Let us call this as h_2 .

The heat generated in the chemical reaction provides for h_1 and h_2 under adiabatic conditions. We therefore equate 28600 to $h_1 + h_2$. The only unknown is the value of T_f which was in the expression C_p for H_2O vapor into T_f minus the boiling temperature of water because all other quantities are known. We can thus get the value of T_f in °C and convert it to K. This is how we calculate the adiabatic flame temperature.

What is the molecular mass? Well, molecular mass is equal to 18 g per mole and therefore, you can find out the C^* and you can find out the performance of the propellant.

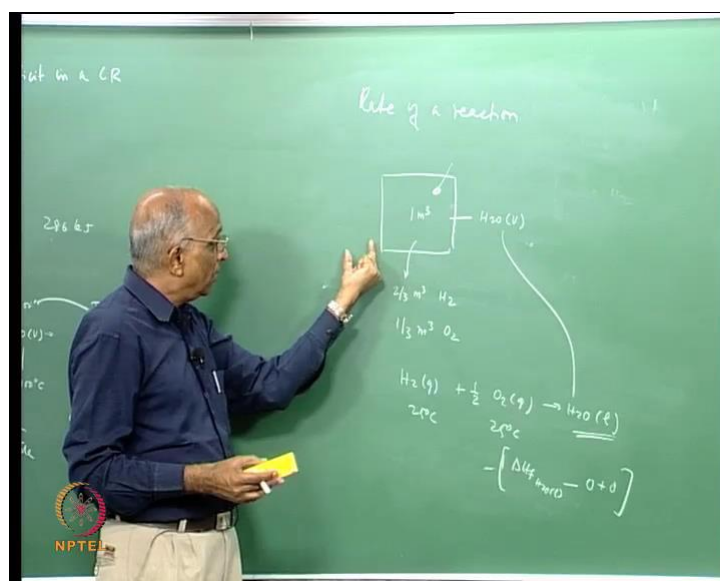
Therefore, for any propellant at any temperature, you have to convert it to the standard and then, evaluate based on the difference at the standard condition between products and the reactant, the heat generated in the reaction and convert the products into something like a final temperature viz., the adiabatic flame temperature. This is how you calculate the flame temperature or the adiabatic flame temperature.

You have a question. I took half mole of oxygen from the initial temperature of 80 K to 90 K. It is the liquid Cp, multiplied by temperature increase of 10 into half mole, convert it to vapor. It is again at 90 Kelvin. This is because we said that the boiling temperature is 90 Kelvin. That means, this should have been at latent heat of vaporization at the boiling temperature of 90 Kelvin. Thereafter the vapor is heated from 90 K to 298 K.

Your question is whether a chemical reaction will take place at 25 degrees centigrade. No, let us be very clear. The reaction need not take place at 25°C. See we are not talking of a chemical reaction at all. We are doing some equilibrium analysis. We say that when a substance gets converted to products, that means the substance which is reacting is at the standard state. It has certain heat of formation. When have products, which are again at the same standard state which is same as the standard state of the reactants. It has some heat of formation. When we go from this structure of reactants to products at the standard state, there is some change in internal chemical energy, which is its heat of formation. Under the standard conditions, there is a decrease in the chemical energy. That energy is the heat of the reaction at the standard condition.

We are not talking of a chemical reactions taking place at 25° or 100° or 200°C. This is just the case, wherein we are equating the change in the chemical energy as the heat: heat = deficit in a chemical energy between reactants and products. This is all what we consider. What is the heat? Deficit in chemical energy, which is the decrease in the heat of formation? It ultimately comes as the heat of combustion because this deficit goes to heat. The products are formed at high temperature from the heat release in the reaction. We are not telling about rate of reaction that comes through totally different source such as chemical kinetics and concentration.

Let me take one example. If I have a tank, let say this is a tank. This tank has a volume of let us say 1 m³. Into this tank I add hydrogen. The amount of hydrogen I add is let us say two-thirds of the volume i.e., I put 2/3 m³ of hydrogen at atmospheric pressure. I also add 1/3 m³ of oxygen at atmospheric pressure. I mix the two. Nothing is going to happen at 25°C.



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The gas is at one atmospheric pressure and 25°C. We are not going to get water at all. But if I were to overcome by initial barrier say increasing the temperature by supply of energy. What is the initial barrier I am talking of? Both hydrogen and oxygen have some energy levels near a datum and if we excite it or activate it. That means I provide ignition energy to get the reaction going. After the reaction is over we form the products.

That means we have to supply some ignition energy to it. Therefore, I put a spark and I create a high temperature environment and then what is happening because of this high temperature; we make hydrogen and oxygen react. May be we have to go into chemical kinetics and may be let us see if we should do it later. Therefore, this reacts and forms H₂O, which is in the vapor state because high temperature gases are formed.

Then, what is it that we do? We cool the products of combustion into something like we form it as water at the standard state and now we find that the change in the energy for this is corresponding to – (the heat of formation of the product minus the heat of formation of the reactants). I am not talking of reaction taking place at any temperature. All what we say is heat of formation is at a standard condition and at this standard condition so much heat is formed. What is the mechanism of temperature increase? This heat goes to increase the products to the higher temperature and if the reactants are at different temperature, again it supplies or removes the heat such that the reactant is at the same standard condition.

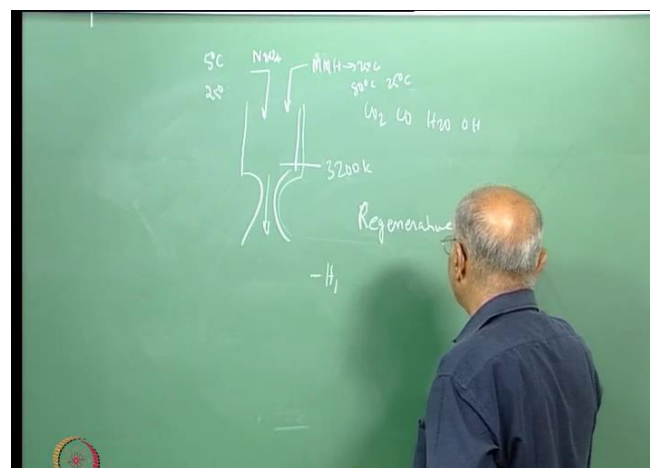
A word about pressure: since we are considering ideal gases, the enthalpy is independent of pressure and it therefore does not enter the calculations for a given substance. The amount of species formed depends on pressure as we discussed under dissociation.

In most of the rockets, say liquid propellant rockets we will see when we supply fuel and oxygen into the combustion chamber. We could have mono methyl hydrazine as a fuel. N_2O_4 could be the oxidizer. You mix the two and burn them to generate hot gases. If you calculate the temperature, the temperature may be something like 3200 K and this hot gas is expanded through the nozzle.

What are the products you are getting? You have carbon and hydrogen in the reactants. You could get CO_2 , you get CO , you get may be some dissociated species, you get water, you have OH . These are the products you get. Now, you know the chamber runs hot. Therefore, you rather take the fuel and instead of injecting it into the chamber directly you use it for cooling the chamber. The fuel then gets pre heated. Instead of the fuel being injected at room temperature we inject it at a higher temperature of something like $80^\circ C$.

I use the liquid fuel to cool the chamber and then inject it. Now, it is at a higher temperature. Therefore, it has higher energy and this energy also contributes to an increase of the temperature of the products. Therefore, in this case we get h_1 to be negative because this is bringing in more heat into the combustion and adds to the heat of formation.

Similarly, N_2O_4 may be at a temperature of something like $5^\circ C$ instead of being at $25^\circ C$. Therefore, heat has to be supplied to make it 25 degree centigrade. Heat has to be added to make it to 25 degree centigrade and therefore, I have less heat here which goes to decrease the effective energy release for the high temperature. (Refer Slide Time: 33:55)

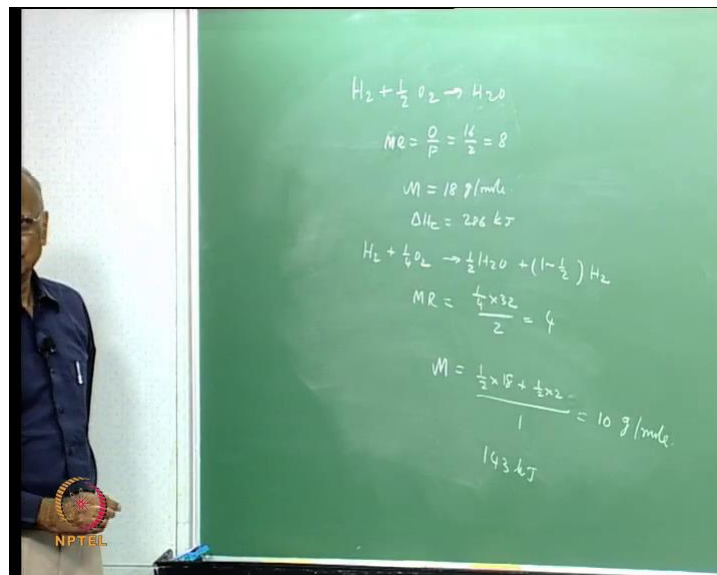


In fact, by preheating using the hot chamber, we are using a regeneration process. We are reusing the heat from the hot combustion chamber and such type of cooling is known as regenerative cooling. We will address this later.

Therefore, we know how to calculate the properties of the products for a set of propellants, which have their initial conditions different from the standard conditions. What is the heat liberated? We did a set of calculations for hydrogen oxygen at stoichiometric mixture ratio, which gave H₂O. The mixture ratio was mass of oxygen divided by mass of fuel, which was equal to 16 by 2 which is equal to 8.

What is the molecular mass of the products; 18 gram per mole. Supposing we have to consider a fuel rich reaction H₂ plus we cannot have ½ O₂. Maybe I have ¼ O₂. In this case, what is going to happen? Let me just have guess over here. I cannot form H₂O because I have only quarter mole of oxygen. Therefore, I form ½ mole of H₂O. We get the balance hydrogen. What is there is 1 – ½ mole hydrogen which is left. Please check. What is the mixture ratio of this reaction? It is equal to (¼)×32 ÷ 2, which is equal to 4. Is it not?

What is the molecular mass of the products? We have half into H₂O: (½)×18 + ½ × 2 = p 10. What is the energy liberated in this reaction? If it was stoichiometric, what is the energy liberated in this reaction? Let us put that number down. Also, what is the heat of formation of water? –286 kJ/mole. Therefore, the heat of reaction in this case is equal to delta heat of combustion is equal to 286 kilo joules in the case of stoichiometric reaction. (Refer Slide Time: 36:10)



What is the heat in this reaction having mixture ratio of 4? At standard state it is equal to 143 kilo joule and this came as half of 286 since only half a mole of water was formed.

If we consider the reaction of H_2 plus O_2 ; this would give us H_2O plus half O_2 . In fact we are assuming this since the product could get dissociated. Mind you we have to do an equilibrium chemical analysis and find out what are the constituents, but this may not be very bad to begin with.

Therefore, what is the mixture ratio? 32 by 2 which is 16. What is the value of the molecular mass of the products? Yes, we are talking in terms of $18+16 \div 1.5$. This is equal to 2 by 3 into 44, which is equal to 29.3. This is for oxidizer rich condition. We have seen fuel rich and stoichiometric and let us now compare the results.

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Handwritten calculations on a green chalkboard:

$$MR = \frac{32}{2} = 16$$
$$M_p = \frac{18+16}{1.5} = \frac{2}{3} \times 34$$
$$\frac{68}{3} = 23 \text{ g/mole.}$$

Fuel - stoich - oxidizer

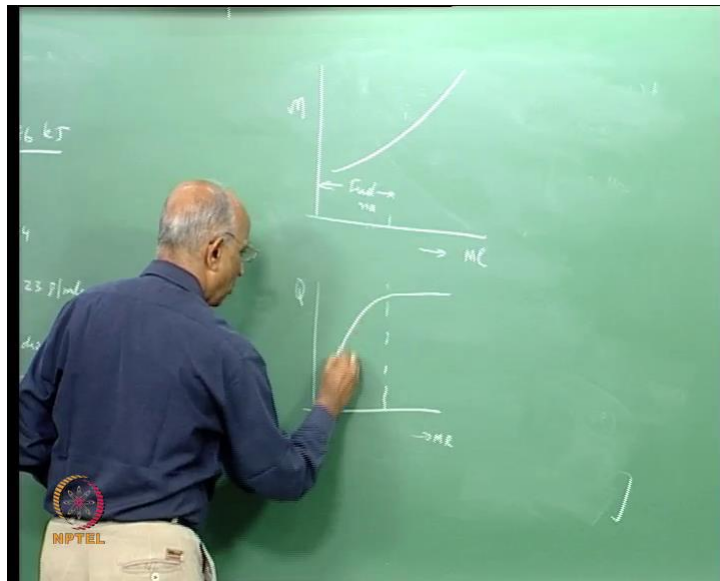
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NPTTEL logo is visible in the bottom left corner.

What happens to the molecular mass? As we go from fuel rich to stoichiometric to oxidizer rich, we find that for oxidizer rich is 23 , for fuel rich it was around 10 and for stoichiometric, it is 18. Therefore, molecular mass is the least for the fuel rich condition.

We find that the heat release comes down when we go from the stoichiometric to fuel rich condition. The heat release for oxidizer rich is same as stoichiometry because oxygen does not matter. It is again 286 kilo joule for this reaction, but if I were to put it in terms of per unit mass or per unit mole, I have half mole increasing over here and therefore, heat release per mole comes down.

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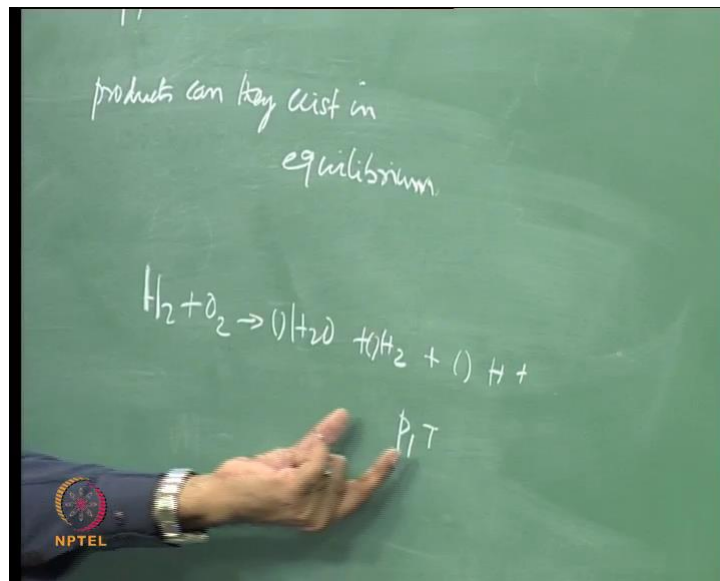


Let us plot the general results. What is it we get for the hydrogen oxygen reaction? We get the molecular mass as this is stoichiometric. This is fuel rich condition. Now, for fuel rich it is less and increases for oxidizer rich condition. The q value for stoichiometric mixture ratio is here; It is constant 286 here. It drops if we were to put it per mole, moles keeps increasing in this direction because I add more and more oxygen and therefore, if we plot heat release q per mole, the value decreases.

Therefore, it is better to operate under fuel rich condition. We learnt how to calculate the temperature. Let us now go to the next part namely, how do I calculate all the products and the heat release in a better way. We need to consider chemical equilibrium. What do you mean by chemical equilibrium?

At a given value of chamber pressure, at a given value of temperature, products of combustion are formed. Can they exist in equilibrium? Can the products exist in equilibrium? What is the composition of the products? Supposing, I react hydrogen plus oxygen at stoichiometric conditions. Is it that only water will be in equilibrium or is it some hydrogen will also be in equilibrium with it? If so, how many moles of water? How many moles of hydrogen? How many moles can stay together at this specified value of pressure and temperature? This is a much better way rather than assuming hydrogen is more reactive and therefore, first it reacts and then, carbon reacts. Why not we do the real analysis and this is what we say as chemical equilibrium analysis.

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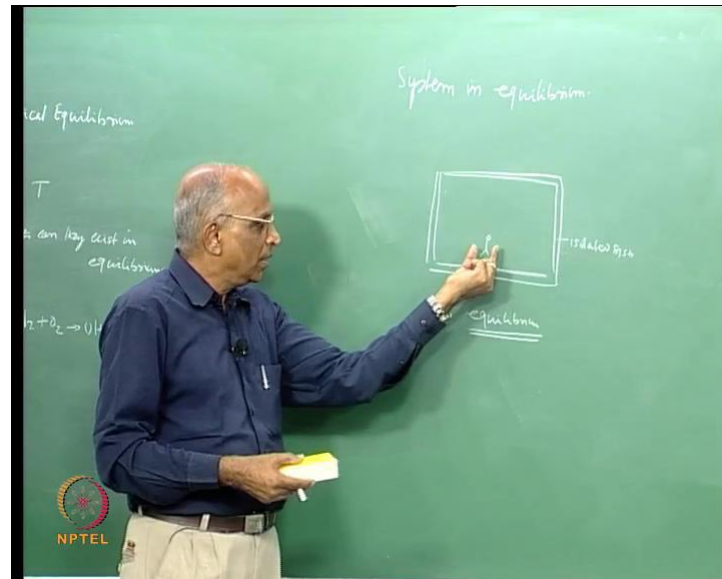


To be able to do the chemical equilibrium analysis, you must first be clear about equilibrium. I think we talked about it in one of the classes. What do you mean by equilibrium of a substance or a system being in equilibrium at a given temperature and pressure? How do you look at it? Let say first take a general example.

Supposing, we consider this room as a system and let us say this room is beautifully insulated. Nothing can come in, no power can come in, no mass can come in, nothing will come in. What is the system we are considering? The system is may be all these lights, may be all of us, may be these chairs, which are the attributes of the system. Therefore, I consider this room as a system and then, we say it is totally isolated. That means I consider an isolated system. I allow the attributes of this isolated system to be there for infinite time, long time. What is going to happen? No change is possible. Everything is finished. All of us have spent such a lot of time with nothing. All of us are in the dead state.

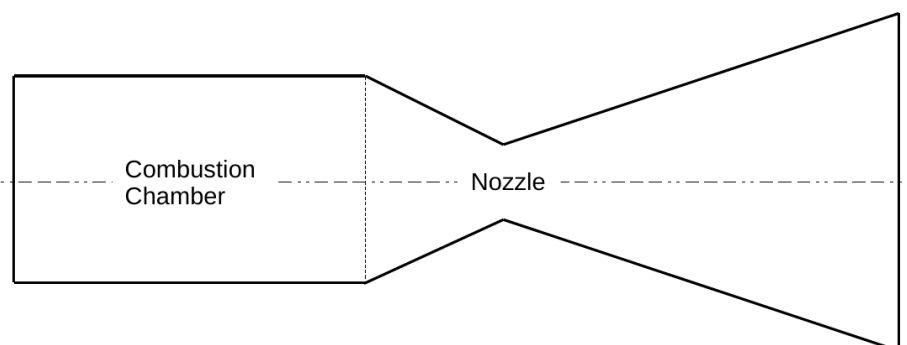
This final state of a system wherein no further changes are possible is what we call as equilibrium. No more changes are possible. Therefore, the concept of equilibrium is very profound in thermodynamics. We tell ourselves, no further change in the state of a system is possible. Why do we say that? Because we have prevented any further changes taking place. May be for sometime it evolved, but afterwards there is no change possible. Therefore, this final equilibrium dead state is when no further changes are possible. We call it as equilibrium, but even though I say it takes infinite time for a system to reach equilibrium, it takes very few nano seconds or a few milli seconds for a gas to reach the equilibrium state.

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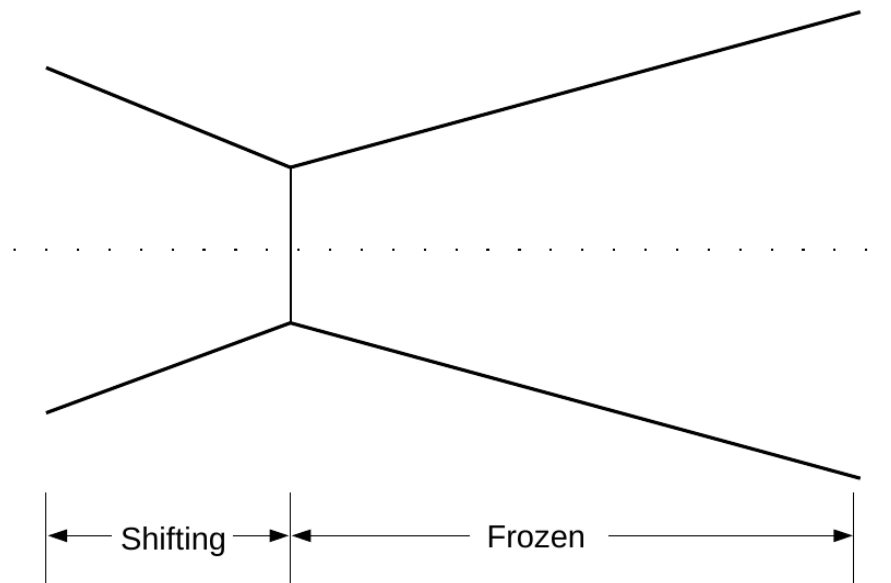
Therefore, it is not necessary that I allow infinite time, but to be able to appreciate the problem well, an isolated system left to itself for long time, reaches us state of equilibrium. Having said that, how do you define equilibrium? No further changes.

In the context of the performance of a rocket, we consider the rocket combustion chamber where the propellants burn to form products of combustion. The velocities in this region are small so that there is adequate time for the combustion to take place. We say that that the residence time or stay time is significant for equilibrium of the process or chemical equilibrium to take place. We calculate the products based on equilibrium.



However, when the products of combustion are expanded in the nozzle, the flow accelerates. The flow velocities, we have seen, are subsonic before the throat in the convergent portion and supersonic in the divergent portion.

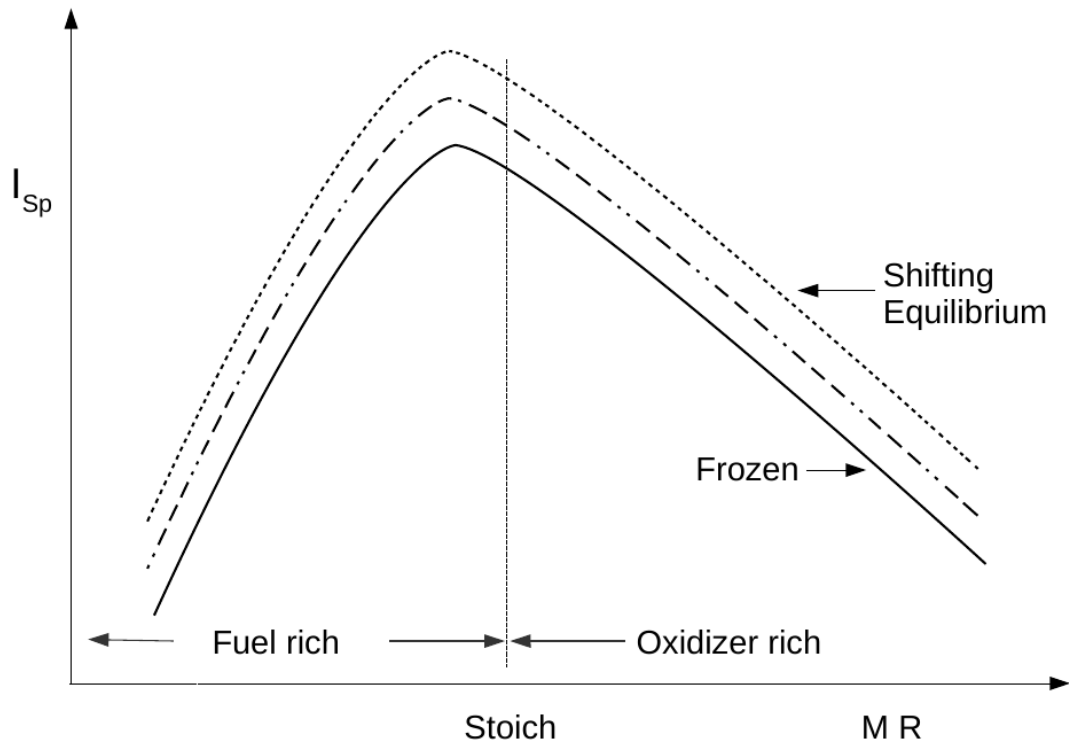
In the convergent portion where the velocities are less than the sound speed, the residence time is still significant and we can presume that chemical equilibrium will prevail. But in the divergent portion of the nozzle, the flow is at Mach number greater than 1 and the flow velocity is greater than the local sound velocity. The flow has also expanded; i.e., the temperature of the gases have reduced. Considering the small residence times and the lower temperatures, equilibrium or complete combustion is not possible. The products remain the same as before or the composition is frozen.



The flow in the nozzle is such that the composition keeps shifting with the temperature change in the convergent i.e., we have shifting equilibrium in the convergent whereas it tends to be frozen in the divergent.

When we calculate the nozzle performance i.e., the exit jet velocity V_J or equivalently the specific impulse, we presumed the specific heat ratio γ and the molecular mass of the products, etc., are constants. This implies that the composition of the gas remains fixed or frozen. We found that I_{sp} is a maximum in the fuel rich region.

If the composition shifts throughout the nozzle, i.e., we have equilibrium, which results in shifting composition, further reactions take place and heat gets released from the recombination of the dissociated gases. Hence the performance viz., I_{sp} predicted by the shifting equilibrium will be higher. The specific impulse obtained assuming shifting equilibrium flow in the nozzle will be higher than if frozen flow is assumed in the nozzle.



But then we also observe that we could have frozen flow in the divergent and hence the actual specific impulse would be in between the two. This is shown in between the two by the dotted line. This is observed in practice.

We could reasonably assume that in nozzle flows, we have shifting equilibrium in the convergent and frozen composition in the divergent. But then this is not true for all propellant compositions and depends on the product gases generated.

This is all what would like to discuss in analysis of performance and prediction of performance.

Thank you.