Rocket Propulsion

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Module No. # 01
Lecture No. # 17

Performance Prediction Analysis

Good morning. I think in the class today, we will extend a little bit of what we did in the last class namely, look at the reaction of hydrogen and oxygen to form water. Why I say we look at this example is when we use hydrogen as a propellant is not as a gas, it at a very low temperature. Similarly, oxygen is at the low temperature.

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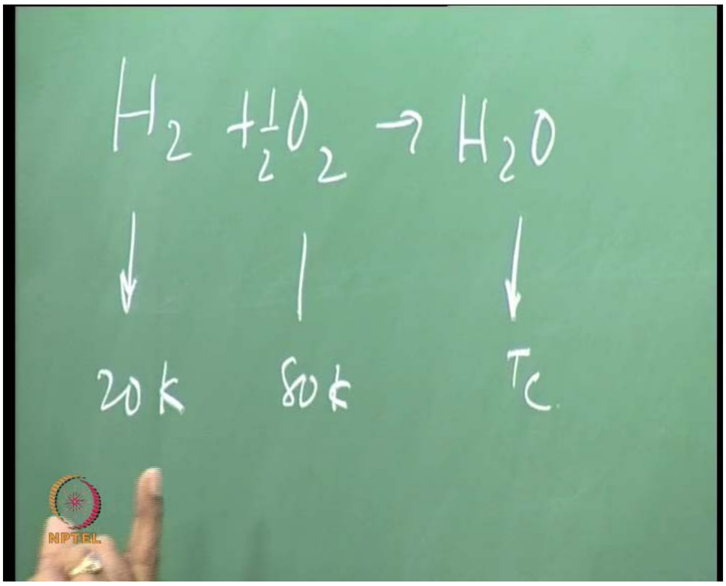

We use hydrogen at a temperature. If it is to be a liquid at 20 k oxygen at let us say 80 k our interest is to form is to determine what will be the temperature of water which is formed. Mind you, as per these reaction is H2 plus half O2 is equal to H2O when the initial condition of hydrogen and oxygen is not standard, when there is some change. Therefore, may be let us do this problem, but before we do this, let us again be very clear of our summary of events what took place in the last class. We told ourselves, well the value of c star is maximum when the mixture ratio is less than mixture ratio storchio metric. That means in this region of fuel rich condition that means fuel rich, we have higher value of c star compared in the oxidizer rich condition.

It is very rare. It is almost impossible to operate an engine 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, but may be before I go to this problem, since we studied what are the conditions required, let us just put down some five or six propellants which we can say are viable propellants. One is we say yes hydrogen and oxygen to give me H2O, but I want to operate it under fuel rich conditions. Therefore, I will get something like H2O plus H plus O plus OH and so on because I get H because I do not have sufficient oxidizer to form water and these are my products of composition which I will get.

Therefore, I say the hydrogen oxygen could be one of the propellants and let us do a small problem under storchiometric and then, extend it to fuel rich condition. The other propellant we said could be hydrogen N2 H4. We said oxidizer could be nitric acid HN03 or better still compared to nitric acid, we said N2O4 had a small positive value. Therefore, hydrogen and N2O4 is a good combination and this would again give me may be some products. Why not we think in terms of kerosene? Kerosene had a large negative value, but not very large. Either, it has something like minus 200 and odd and you had oxygen, it gives me products. Again I choose fuel rich condition and this could be candidate which we could have.

You find that these substances like nitric acid may be N2O4 are widely used as oxidizers. Hydrogen is also used and we will see the advantages of using hydrogen with this. Instead of hydrogen, I could have something like N2 H4 which is hydrogen. I remove one of the hydrogen atoms here, I have N2H3. I substituted with the metal radical and it becomes one metal with hydrogen. It is known as mono metal hydrogen and this is very popular propellant combination mono metal hydrogen plus N2O4 giving me products of combustion. Mind you, we will again keep it to be fuel rich, not oxidizer rich like this. We can keep on adding. Most of these things are may be gaseous propellants. I could liquefy it and use it as a liquid propellant.

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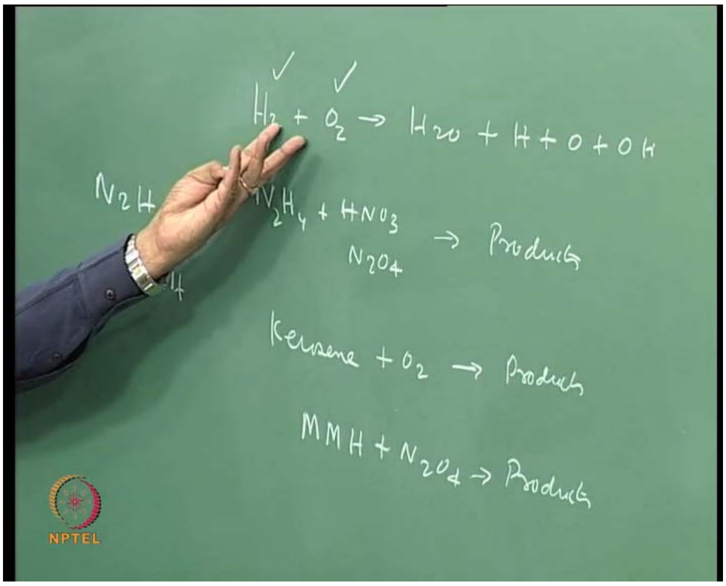

These are all liquids and we could have solids. What could be the solid? We say I could use something like let us say, we had ammonium per chloride which was an oxidizer plus aluminum plus. We also told ourselves in the last class, may be nitro cellulous could be used or else polymer could be used and you know we normally do not combine ammonium per chlorate aluminum and nitro cellulous or rather we combine nitro cellulous and nitro glycerin to give me a propellant. We combine ammonium per chlorate plus aluminum plus polymer to give me a solid propellant.

Well, the selection is somewhat limited. We cannot have infinity because based on the criterion, we have let down. We said yes, this becomes something like a double base, two bases. Each one could be a propellant, but this could be a propellant or I could have composite of ammonium per chlorate aluminum and polymer to give me something like a solid propellant.

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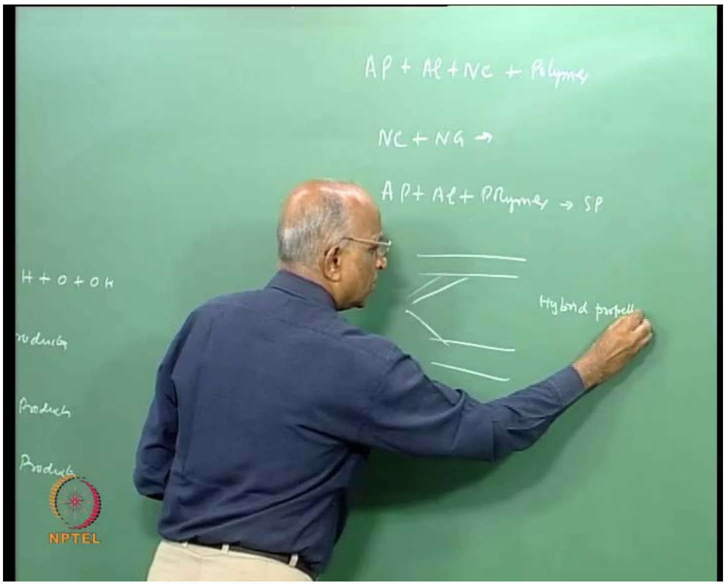

If I think in terms of hybrid, well I take the polymer. I cast it over here. I allow the acid to fall on it, liquid and solid and this gives me what we call as a hybrid propellant and again, we make sure that the rate of reaction is such that it will still be fuel rich, such that I get a high value of performance. This is all about propellants (( )), but I think we have to get into some more depth of why if the initial conditions are different, how do you get the temperature of this, but one thing which I forgot to mention in the last class was if I have pressure in the chamber like let us consider the following.

I have a chamber in which chemical reactions are taking place. Supposing I have a high pressure, very high pressure here, if I have high pressure in a chamber, the amount of dissociation what takes place, what means dissociation is may be CO2 becoming CO plus O or rather let us say, CO plus half O2 or CO plus O or let us even say CO plus O. You know if I have high pressure environment, I cannot increase the number of molecules to make something dissociate at high pressures is more difficult than at low pressures because what the pressure do, it tries to reduce the volume. That means if I have to grow the volume because molecules are increasing, I essentially need low pressures.

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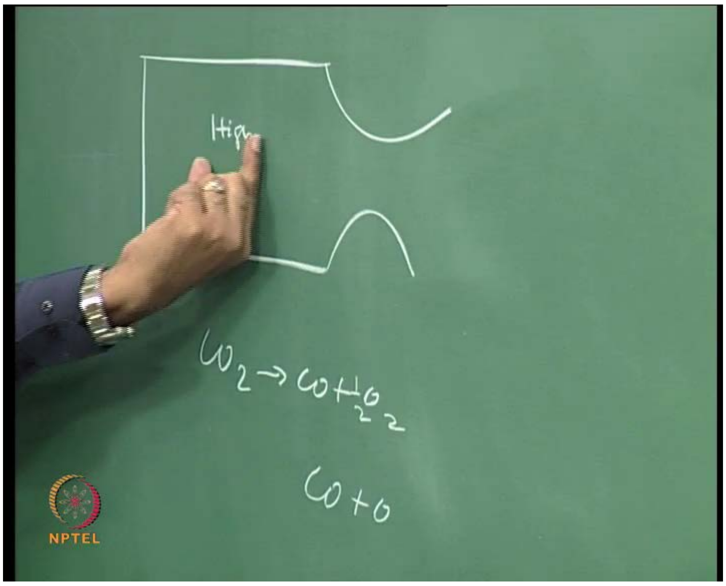

Therefore, I have still not considered the effect of pressure. It must come from dissociation, but having even without doing this, let us see some results on what will be the effect of let us say dissociation. All what I am trying to say is a dissociation reaction. What do we mean by dissociation? We are talking of breaking up. 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 CO2. It is trying to break up into C plus CO plus O. Let us say you know when this breakup will be possible. At extremely high temperatures, at the temperatures in which may be operating, but more of more interestingly, if I have a high pressure, the pressure will try to snuff. This reaction amount of dissociation will be much less at high pressure than at low pressure because at low pressure the ambient pressure is small, something can dissociate and multiply.

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 dissociation, T c will be higher not only dissociation, but since dissociation is small, the molecular mass will also be large, but the effect of T c is much more dominant and therefore, may be it still has an effect on c star.

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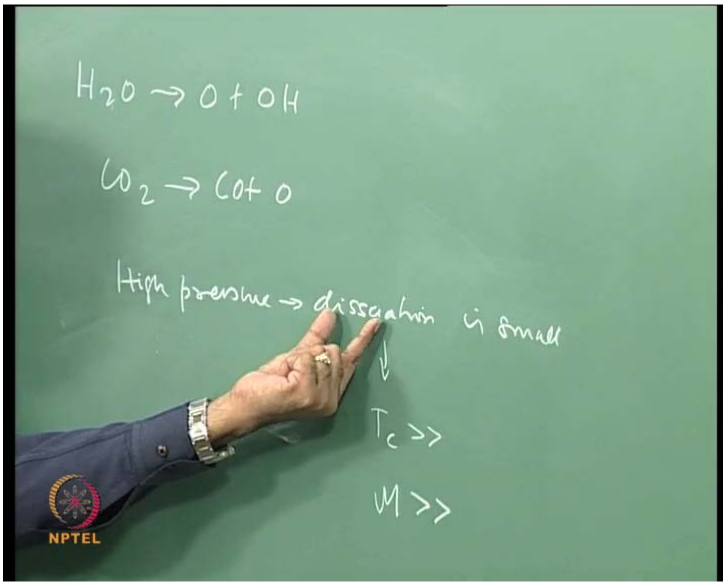

$H_2O \rightarrow O + OH$

$CO_2 \rightarrow CO + O$

High pressure → dissociation is small

$\downarrow$

$T_c >>$

$M >>$

Let us take a look at the result. Before I do the theory part of it, you know here I plot 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.

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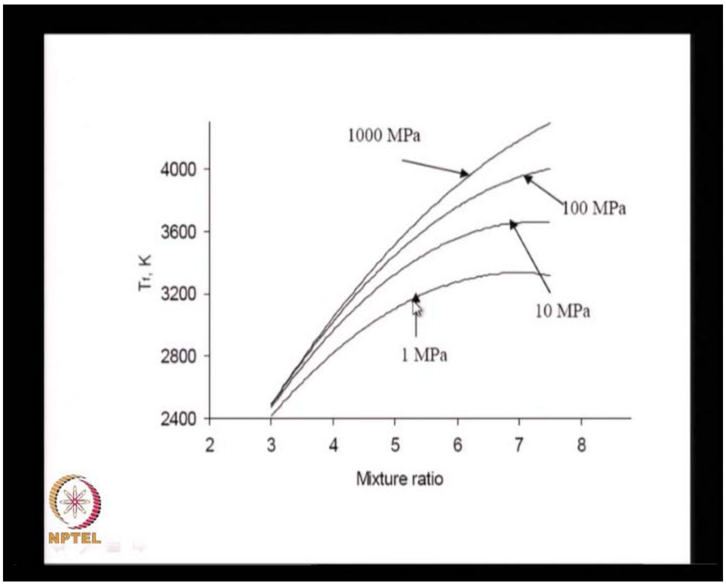

You find that at a given mixture ratio, as the pressure increases, the temperature increases because at high pressure, the amount of dissociation is less. We have to find out why we will do a problem.

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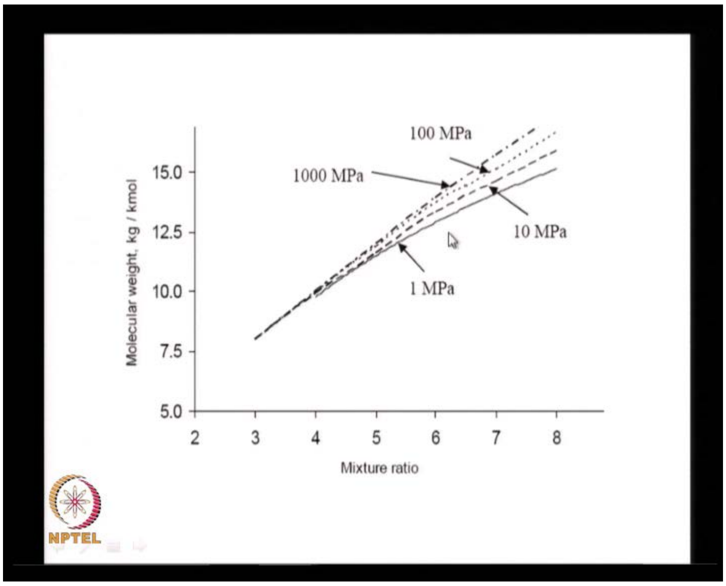

You also find that the molecular mass of gases increases with mixture ratio, but also we find that as the pressure increases, the molecular mass increases. Why is that? At higher pressures we have less dissociated gases and dissociated gases have a low molecular mass. Is it clear?

Let us go to the next one. If now I say the value of gamma, we said gamma is higher for the mono atomic specius, 1.67 for helium for very complicated c c l for it is 1.18 or something 1.13. Therefore, you find that as the chamber pressure increases, the dissociation is less and therefore, the gamma value is smaller and of course, with 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 is that? Because I have more complicated molecules, dissociation is less and now, if I put all the things together, I find my effective c star are equivalently the I s p because the I s p is equal to c star into the nozzle performance is equal to you find that as pressure increases, the optimum value of the mixture ratio for which I get the maximum value of c star keeps changing.

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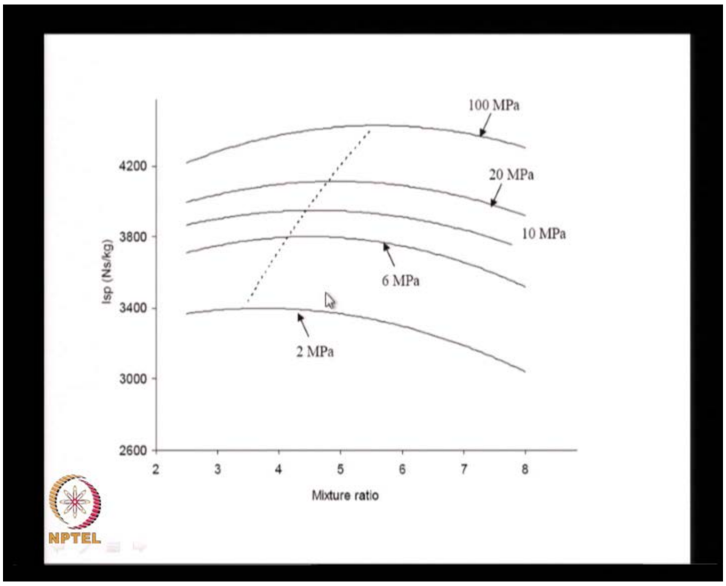

Therefore, there it is not only just the mixture ratio alone which decides it, but the pressure is important because pressure influences the amount of dissociation. This is for hydrogen oxygen propellant combination. Therefore, we have to take a look at dissociation and these are results for which we are not yet equipped to do the analysis, but we will be doing it. Therefore, go with this background into what happens when I have a reaction, stoichiometric reaction of hydrogen plus half oxygen. Let us say forming water, my aim is to find out the temperature of the combustion products.

How do I do this problem? We would first like to understand what is the heat generated in this reaction, but mind you hydrogen and oxygen are not at the standard state of 298 Kelvin, but hydrogen is a liquid. I use it as a liquid at 20 Kelvin; I use oxygen at 80 Kelvin instead of 298. Therefore, I have to first convert these two substances which are at reduced state, reduced temperature to something like 298. 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.

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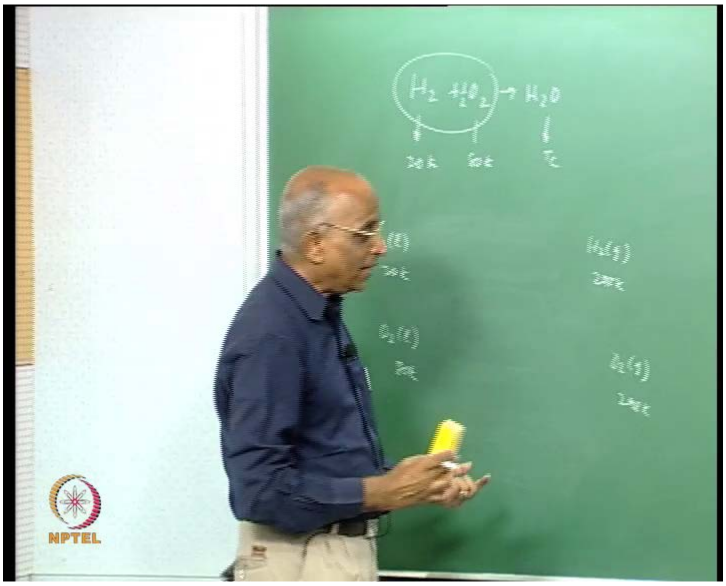

Similarly, I would try to take oxygen which is now a liquid at 80 Kelvin, convert it into hydrogen. I am sorry oxygen has a gas at 298 Kelvin. Once I have converted this, then the standard heat of formations I can use. What is it I can do? I can thereafter take this oxygen which now I have converted to 298 which is gas hydrogen which is a gas at 298 Kelvin. From this I can get water H 2 O which is again a liquid at 298 Kelvin.

Now, what happens is some heat is generated in this reaction. This heat takes the water. That means H2O has a liquid at 298 Kelvin and converts it as H2O as vapor at high temperature T f and this is what I want to find out what is my temperature.

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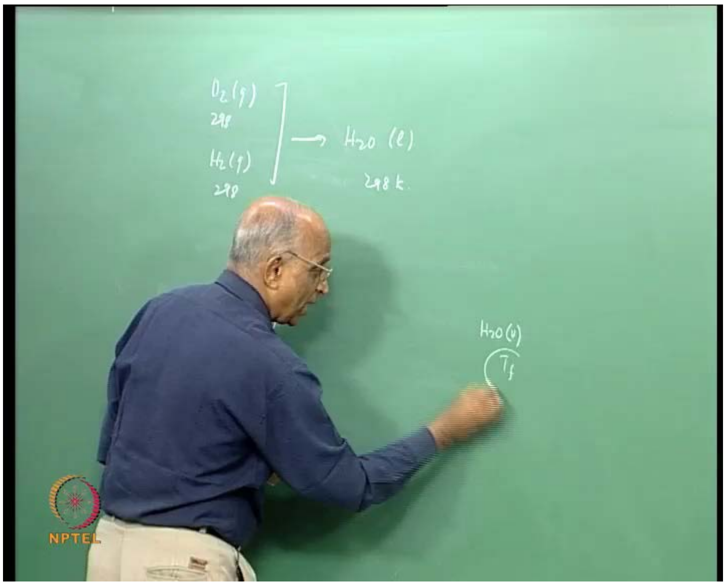

Therefore, I have to go through this process. What is it? We call temperature if it is adiabatic; we call it as adiabatic flame temperature. Therefore, we would like to find out the adiabatic flame temperature of the products of combustion when the reactance are not at the standard state, but in a state of liquid at low temperatures and this is what I want to do.

Therefore, what is it I 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 may be of hydrogen is around 22 Kelvin. That means this is sensible heat wherein I still have the liquid phase and then, once it has reached the boiling point at 22 Kelvin, I supply the latent heat or heat of the vaporization and convert it to H2 vapor again at the boiling temperature itself. It is a constant temperature process and once it has reached T b and we said T b, we are assuming it to be 22 at the particular pressure. Once it has become vapor, again I have sensible heat. I increase the temperature from 20 to 298 Kelvin.

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 now know this. Therefore, I can say oxygen is a liquid at the temperature of boiling, temperature of oxygen is around 90 Kelvin and then, I convert it using latent heat into oxygen gas oxygen vapor. Then, I convert at the boiling temperature of 90 Kelvin I have to increase it to 298 Kelvin.

What is the process here? I have liquid which is formed at 298 Kelvin. Mind you, 298 Kelvin is 25 degree centigrade. I have to convert it to water again at the boiling temperature of water. Let us assume, it still 100 degree centigrade and at 100 degree centigrade what I do? I have vaporization, that is latent heat taking place and I form water which is a vapor. Now, this conversion is again at 100 degree centigrade vapor and then, I convert the 100 degrees centigrade to something like T f.

Therefore, the heat which is generated by the reaction at the standard state should be able to supply heat for this conversion plus taking the water to this particular temperature. Therefore, let us write the equation. I think this energy equation is very important because I do not think there we use propellants at always at 25 degrees. Sometimes in a cold condition like for instance, whenever we use N2O4, we chill the N2O4 and use. Otherwise, it tends to vaporize. Therefore, we have to consider this and a classic example is these low temperature propellants. That is what I thought I should do this.

So, can I start with the problem? Is the thing clear? All what I am trying to say is all what we studied so far was the substance is originally at the standard state and the products are also formed at the standard state and we calculated the heat which is generated at the standard state.

Because we just said yes, we had one mole of H 2 O into delta h f corresponding to H 2 O which was something like 286 and minus the heat of formation of the reactant was 0 0, that is 0 plus 0. We found out what is the decrease and we said H 2 O is equal to something like 286 kilo joule per mole and forming one mole. Therefore, the heat generated is equal to 286 kilo joule in this reaction.

We never bothered about the heat of this which goes into this. For the heat to calculate this temperature, let us do it. Therefore, let us put the data more clearly. I just put down the data together. I think data is important. We have hydrogen as a liquid, the boiling temperature is 22 and we need for this change, we need the specific heat of the liquid hydrogen. Then, let me put it down here specific heat of l H 2 is required and this specific heat of l H 2 is equal to 20 joule per mole. The latent heat of conversion of liquid hydrogen to hydrogen to hydrogen vapor at the constant temperature of 22 Kelvin is equal to 890 joule per mole. I prefer to use mole as the unit of the matter of substance because it tends to be simpler because always chemical rate equations are written in terms of moles and conversions become simpler.

Similarly, if I have for oxygen, the specific heat of liquid oxygen is equal to 29 joule per mole. The latent heat that is equal to h f g is what we normally use. H f g for oxygen is equal to 6800 compared to 890. We need two more things. We need the specific heat of oxygen as it increases in temperature between 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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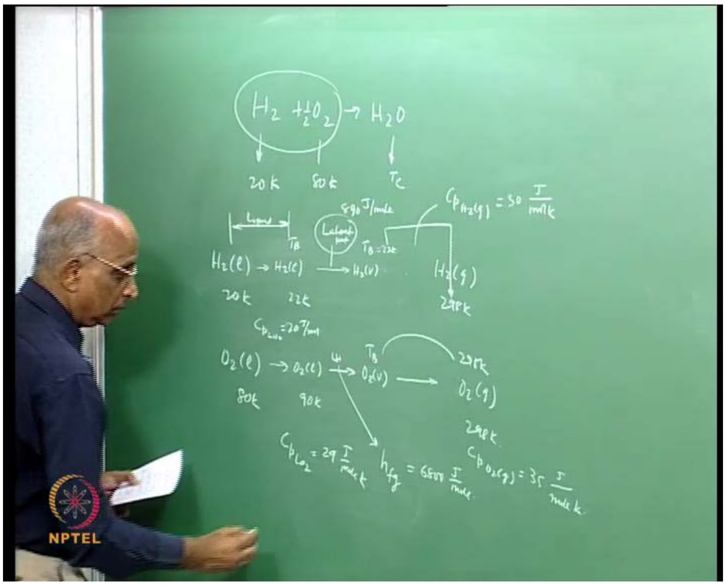

The specific heat of hydrogen as a gas is equal to 30 joule per mole Kelvin and the specific heat of oxygen is equal to something like 35. We should have had the word Kelvin here. Whenever we have specific heat, we are talking per unit temperature change and similarly, when we talk in terms of water to this here, you are talking out specific heat of water. As a liquid latent heat of water over here, you are talking of specific heat of water in the form of a vapor.

Then, let us put down these values. Liquid is equal to 90 joule per mole Kelvin, the conversion of h f g for water is equal to 35. Again I think we will have to check these numbers. Yes, 35000 joule per mole and specific heat of vapor is equal to something like 58 joule per mole Kelvin.

How do I do this problem? When I have the heat coming out under standard conditions, all what we are able to write is if H 2 is at 298 Kelvin and it reacts with half of oxygen, again at 298 Kelvin I form water one mole of water at 298 Kelvin. In this case, the heat of formation of water is equal to minus 286 or I get 286000 joules of energy per mole of hydrogen reacting from standard heat.

Now, what is happening? Let us say, let me put this in a better form. Let us to make ourselves doubly clear, the heat given to liquid hydrogen is it starts with 20 k, goes to boiling point at 22 Kelvin. This corresponds to c p of liquid hydrogen into d to plus. I have h f g corresponding to the hydrogen going from liquid to vapor plus I have between 22 to 298. The value of c p corresponding to gaseous hydrogen d t plus. Let me do the same thing 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 into d t plus h f g corresponding to oxygen at 80 Kelvin plus. I have going from 80 to 298 corresponding to c of oxygen gas into d t over here.

Whatever I have written here through arrows have said this and I am also assuming c p to be caused in this particular region and whenever we say c p is constant, we assume it something like a perfect substance. c p does not change with temperature.

Let me not do this exercise by putting the numbers. I will just call it as h1. What is h 1? So much joules corresponding to this may be all calculate and plug in the value of h 1. Now, I want to know the value for water. What happens over here? What happens to water? Again, it has one mole. I think we forgot something. See this is per mole, per mole, per mole is when I have oxygen. It is half mole here. Therefore, I have half mole because h f g was per mole, I have half mole here. Therefore, h 1 should contain half mole of oxygen and one mole of hydrogen over here.

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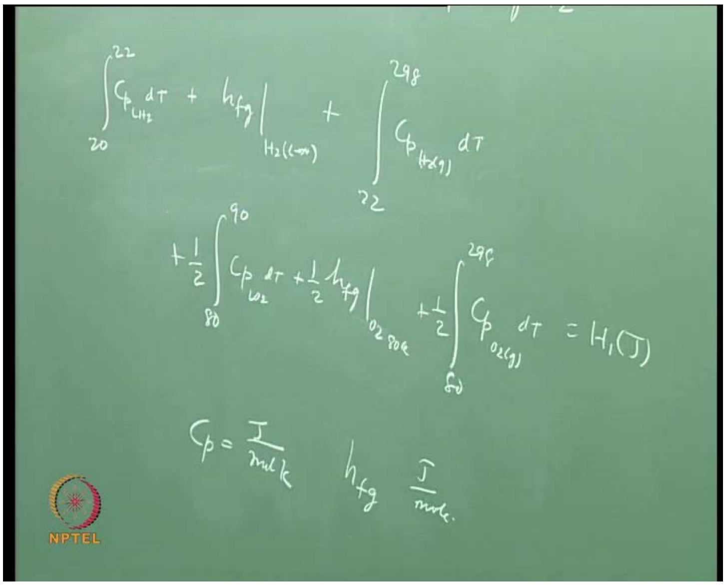

$$\int_{20}^{22} C_{p_{LH_2}}\,dT + h_{fg}\Big|_{H_2(l \to v)} + \int_{22}^{298} C_{p_{H_2(g)}}\,dT$$

$$+\frac{1}{2}\int_{80}^{90} C_{p_{LO_2}}\,dT + \frac{1}{2}h_{fg}\Big|_{O_2\,80K} + \frac{1}{2}\int_{80}^{298} C_{p_{O_2(g)}}\,dT = H_1(J)$$

$$C_p = \frac{J}{mol\,K} \qquad h_{fg}\ \frac{J}{mole}$$

Mind you, we define c p in terms of joule per mole Kelvin. We define the vaporization process as equal to joule per mole. If you are going to use these standard way of looking at 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, but I always find working with moles is to be much simpler.

Now, when I want to use it for water, what is it I do? I again take water is formed at 298. Therefore, you have 25 degree centigrade to I still assume 100 to be the boiling temperature. If the pressure is higher, the boiling temperature will go up c p for water as a liquid which we know into d t plus h f g for water which is given to you per joule per mole plus I have from 100 to the value of t f which the adiabatic flame temperature into c p for water in the form of vapor into d t.

This is all one because I have only one over here. This I call as H 2. Now, what I do is my heat which is generated is equal to 28600 or rather H 1 plus H 2 is equal to 28600 and the only unknown is the value of t f which is equal to c p H2O vapor t f minus the boiling temperature of water because all other things are known. We are able to get the value of t f and this is how we calculate the flame temperature.

What is the molecular mass? Well, molecular mass is this product here. The molecular mass is equal to 80 and therefore, you can find out the c star, you can find out the performance of the propellant. Therefore, given any propellant at any temperature, you have to convert it to the standard and then, evaluate based on the difference in the standard between products and the reactant, the heat generated in the reaction and convert the products into something like a final temperature, adiabatic flame temperature. This is how you calculate the flame temperature at the adiabatic flame temperature.

Which one here? See what is it I have done? I took half mole of oxygen from the initial temperature to 90 degree. It is a liquid c p, allow to t d and then, I take half mole, convert it to vapor. It is again at k at the 90 Kelvin. Yeah, ur because we said that the boiling temperature is 90 ur. That means, this should have been at the standard at the boiling temperature of 90 Kelvin and this goes from the boiling temperature of 90 to 298. This is what it is.

Which one? No, let us be very clear. You are telling me that the reaction need not take place at 25 degree centigrade. See we are not talking of a chemical reaction at all. What is this we are talking? 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. If I have products which is again at the standard state, the same standard state it has some heat of formation. When I go from this structure of let us say, substance which has some internal chemical energy which is its heat of formation, the standard condition it loses some energy. That energy is coming as the heat of the reaction.

We are talking of a chemical reaction taking place at 25 degrees or 100 degrees or 200 degrees. This is just the case, wherein we are comparing what is the heat which is required, heat which comes out, heat deficit in a chemical reaction. This is all what we consider. What is the heat deficit? It ultimately comes as the heat of combustion because this deficit goes to heat, the product at high temperature we are not telling about rate of reaction that comes through totally different source because we must remember one thing. See, whenever we study all these things, we are no longer; we have never said anything about rate of reaction.

Let me take one example. If I were to have a tank, let say this is tank. This tank contains volume of let us say one meter cube. Into this tank I put something like hydrogen. The amount of hydrogen I put is let us say two-thirds of this I put as hydrogen, that is 2 by 3 meter cube of hydrogen at atmospheric pressure I put and into this volume, I also put 1 by 3 meter cube of oxygen. I mix the two. Nothing is going to happen.

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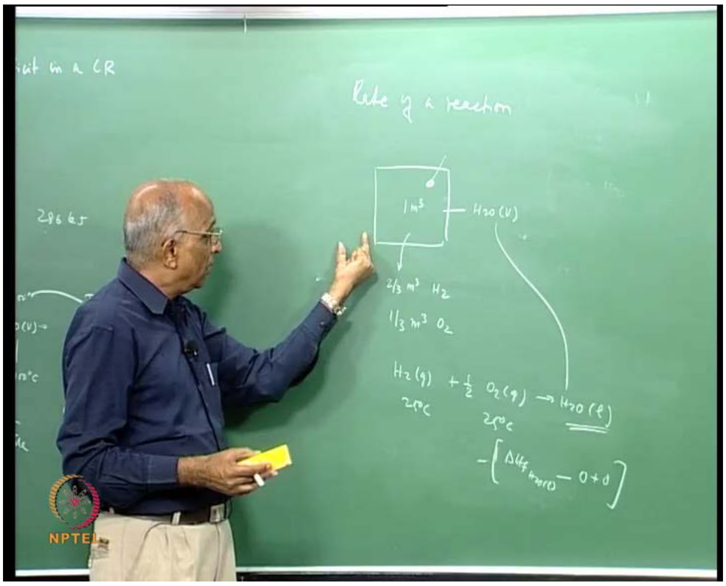

It is at room temperature I have what I have is H2O gas at let us say, one atmospheric pressure 25 degree centigrade. I have oxygen gas half of half of it is oxygen which is again gas at 25 degrees and again the same one atmospheric pressure. Nothing is going to happen. I am not going to get water at all, but if I were to overcome by initial barrier, what is the initial barrier I am talking of. I am telling, yes all these two things are standard like for instance, I have a scale here. That means I am talking of something like initially hydrogen is at this level and oxygen is also at the same standard level. I need to excite it. That means I have to increase the activation energy, such that it goes through this and comes back and forms a reactant here.

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

Then, what is it I do? I cool the products of combustion into something like I form it as water at liquid state and now I find that the change in the energy for this is corresponding to heat of formation of the product minus some of heat of formation of the gases. Therefore, if the product is at the same standard state as this the energy liberated is equal to one of heat of formation H_2O which is in the liquid state minus 0 plus 0 and here, I have minus sign over here and this is the heat which is liberated.

I am not talking of reaction taking place at any temperature. All what we say is heat of formation is at standard products are standard, so much heat is formed. What is the mechanism? This heat goes to increase the products to the higher temperature and if the reactance is at different temperature, again it helps to either if the reactance is at higher temperature; they will give you more energy itself. In fact, if we were to take a case, let us do it away.

You know in most of the rockets, liquid propellant rockets as we will see when we study liquid propellant rockets. You know you do not inject at let us say you have the case of let us say, we have mono metal hydrogen as one of the fuel. You have N_2O_4 as the oxidizer. You mix the two you burn them generate hot gases and if you calculate the temperature the temperature may be something like 3200 Kelvin and this hot gas is expanded through the nozzle.

What are the products you are getting? You have carbon and hydrogen, you get CO_2, you get CO, you get may be some dissociated specius, 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 instead of injecting it into the chamber high rather pre heat. The liquid m h which is coming instead of it being injected at room temperature of 25 degree centigrade, I inject it at something higher temperature of something like 80 degree centigrade.

I use it to cool the valve and then, inject it. Now, it is at a higher temperature than 25 degree centigrade. Therefore, it has higher energy and this energy also contributes to this. Therefore, in this case I get h h 1 will be negative because that is I mean this is bringing in more heat into the combustion and I have heat of formation which helps this.

Similarly, N_2O_4 may be at a temperature of something like 5 degree centigrade instead of being at 25. Therefore, heat has to be supplied to make it 25 degree centigrade. Heat has to be removed to make it 25 degree centigrade and therefore, I have excess heat here which helps in increasing the energy of combustion.

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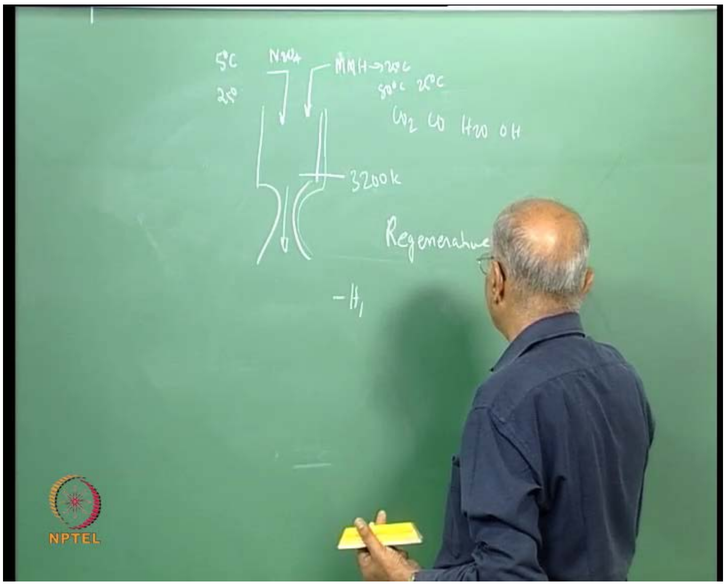

In fact, we are using regeneration. We are reusing the heat from here to be able to do this and such type of cooling is known as regenerative cooling. We will construct this. Is it not? Now, let us go ahead.

Therefore, we know how to calculate for a different set of propellants which are away from the initial, yeah which are different from the initial standard condition. What is the heat liberated? Let us also quickly do since we did hydrogen oxygen, let us take a look at may be have hydrogen oxygen reaction which is stoichiometric giving me H2O and this as a fuel to oxidizer ratio or mixture ratio which is oxygen divided by fuel which is equal to 16 by 2 which is equal to 8.

What is the molecular mass of the products 182 plus 16 18 gram per mole? Supposing I have to consider a fuel rich reaction H2 plus I cannot give half O2. May be I give quarter O2. In this case, what is going to happen? Let me just have something like a guess over here. I cannot form H2O because I have only half of oxygen. Therefore, I form half H2O. No, yes half H2O because I have half of oxygen here and what happens to the balance oxygen. I get the balance hydrogen. What is there is 1 minus half hydrogen which is left. Please check. I am just putting hydrogen plus this. What is the mixture ratio of this reaction is equal to 1 by 4 into 32 divided by 2, which is equal to 4. Is it not?

What is the ma mol? What is the molecular mass of the products? In this reaction I have half into H2O 18 plus half into 2 which is equal to divided by half plus half which is 1. That is 1 which is equal to 9 plus 1 which is 10.

What is the energy liberated in this reaction? If it was of this type stoichiometric, what is the energy liberated in this reaction? Let us put that number down. Also, what is the heat of formation of water? Let us go back 286. Therefore, the heat of reaction in this case is equal to delta heat of combustion is equal to 286 kilo joules.

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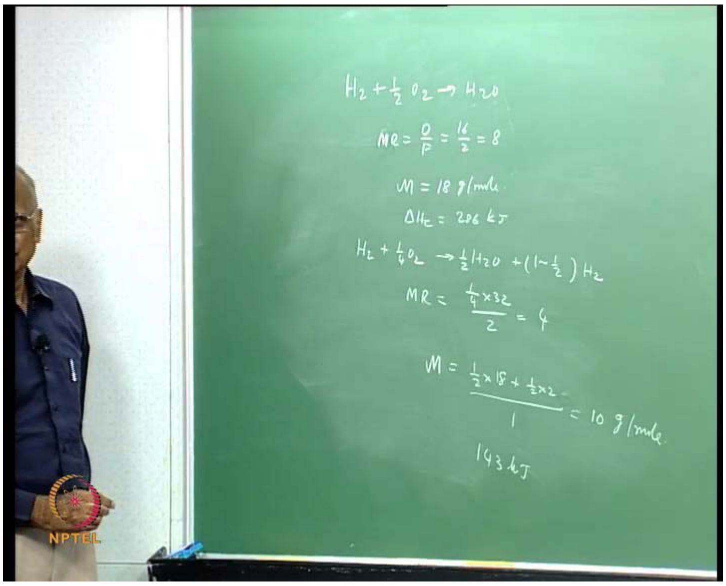

What is the heat in this reaction? 0 0 0. All at standard state which is equal to 143 kilo joule 286 by 2143. Let us consider the reaction of H 2 plus O2 giving me H2O plus half O2. I am just assuming this. Mind you we have to do an equilibrium analysis chemical equilibrium and find out what are the constituents, but this may not be very bad to begin with.

Therefore, what is the mixture ratio? Now, yeah yes correct 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 plus 16 divided by 1.5. 18 plus O 2 is 30 216 divided by 1.5. This is equal to 3 by 2 into 44. That is equal to 66 gram per mole. Am I divided by 1.5? Yeah, you are 2 by 388 by 388 by 3 means 2 6 24 28 gram per mole 24 2 by 3 into 44 34. I am sorry which is equal to 70 68 by 3 23. This is for oxidizer rich, this is for fuel rich, this is for stoichiometric and let us now compare whatever we have done, we can revise it.

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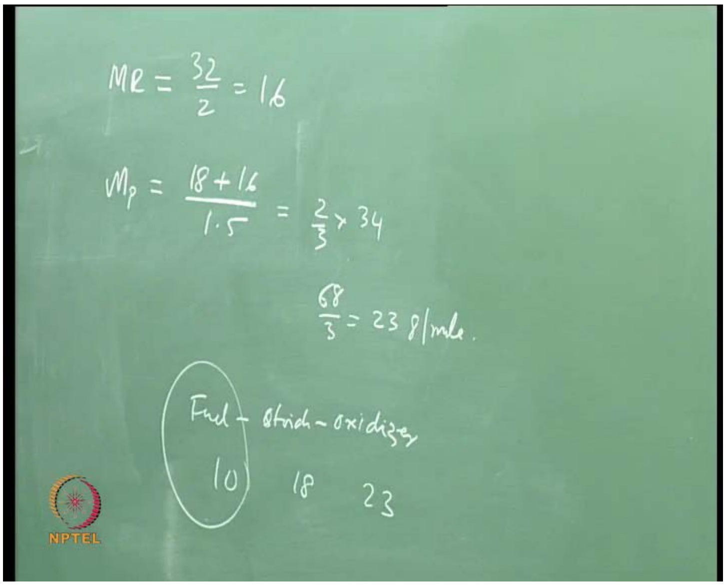

What happens to the molecular mass? As we go from fuel rich to stoichiometric to oxidizer rich, we find that for oxidizer rich is 23, for fuel rich it was around 10 and for stoichiometric, it is 18. Therefore, molecular mass is rich is least for the fuel rich condition.

We find that the heat release comes down when I go from the stoichiometric to this. The heat release for this is again the same because oxygen does not matter at all. 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, cube per mole comes down and this is what we decide it.

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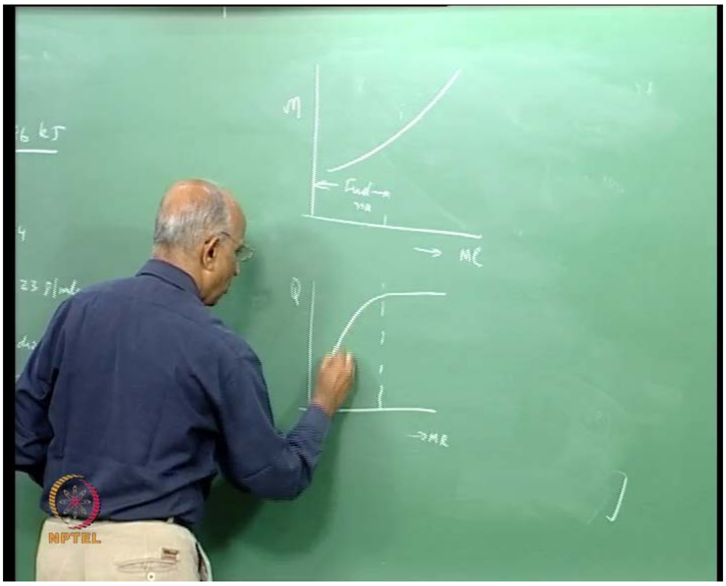

Let us plot that also. Why you leave it half way through? What is it we get for the hydrogen oxygen reaction? We get the molecular mass as this is stoichiometric. This is fuel rich condition. Now, fuel rich is less increases over here. The q value stoichiometric is mixture ratio is here the total heat of the reaction. What is its mixture ratio here? It is constant 286 here. It drops if I were to put it cube per mole, mole keeps increasing in this direction because I add more and more oxygen and therefore, if I have to plot cube per mole, this constant will now become and this is all what we learned

Therefore, it is better to operate it under fuel rich condition. All what we say this is an example of hydrogen oxygen. We learnt how to calculate the temperature. Let us now go to the next part namely, how do I calculate all these things. Supposing, I were to consider chemical equilibrium. What do you mean by chemical equilibrium?

At a given value of chamber pressure, at a given value of temperature, how do the different products of combustion, how are the products? Can they exist in equilibrium? Can the products exist in equilibrium? What is the composition? Supposing, I react hydrogen plus oxygen. Is it that only water will be in equilibrium or is it hydrogen will also be in equilibrium with it? If so, how many moles of water? How many moles of hydrogen? How many moles of H and all 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 you do the real analysis and this is what we say is a chemical equilibrium analysis.

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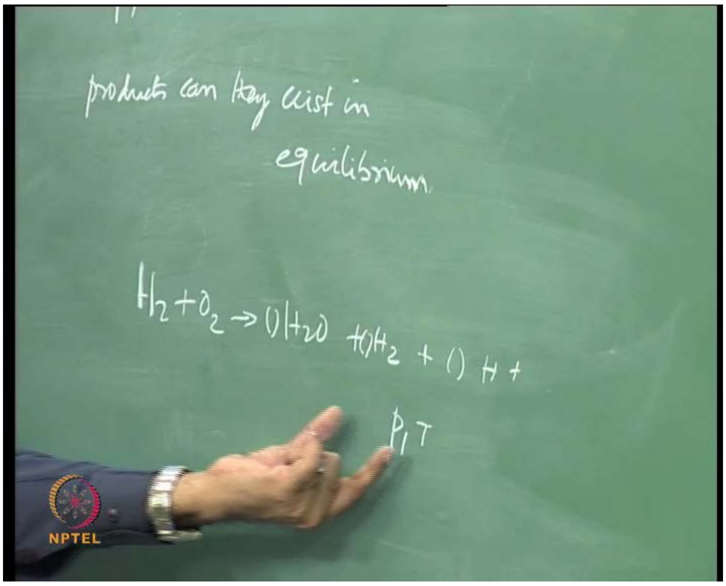

To be able to do the chemical equilibrium analysis, you must first be clear. What do we mean by equilibrium? I think we talk over it in one of the classes. What do you mean by equilibrium of a substance or a system being in equilibrium? How do you look at it? What you understand by equilibrium? How will you define it? I think we should think over it. Yeah. How will you define it? There should be no reaction, but in this case, let us 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, no air 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 state, no further change in the state of a system is possible. Why do we say that? Because nothing you know you have prevented anything from evolving. May be for sometime it evolved and then, it stopped or something, but afterwards there is no change possible. Therefore, this final equilibrium dead state in which no further changes are possible, we call it as equilibrium and so, but even though I say it takes infinite time for gases to come into equilibrium, it takes very few nano seconds or a few milli seconds it reaches that state.

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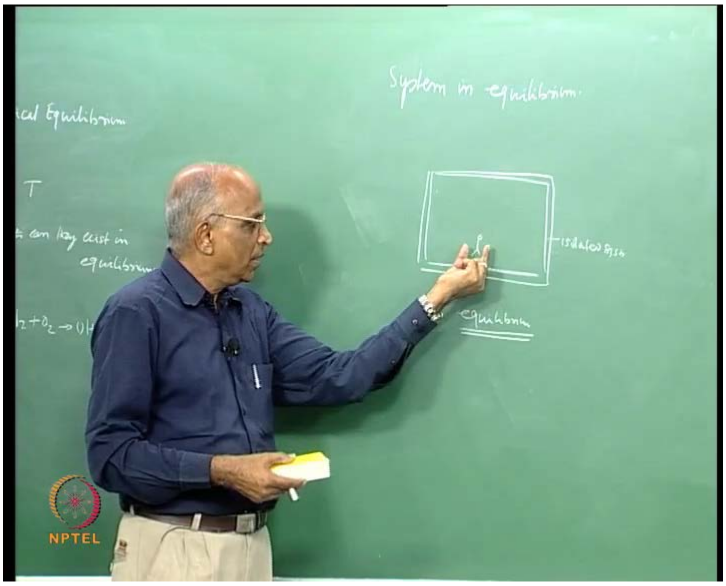

Therefore, it is not necessary that I allow infinite time, but to be able to appreciate the problem well, an isolated system left to itself for long time, reaches us state of equilibrium. Having said that, how do you define equilibrium? How can you achieve equilibrium like for instance, I have let us say products A, B, C in an enclosure. I want these gases which are originally of different levels or something and I have may be NA moles of ANB moles of CNB moles of BNC moles of C. I want to define the equilibrium condition and so, the parameter which is used for defining equilibrium is what we call as gifts free energy.

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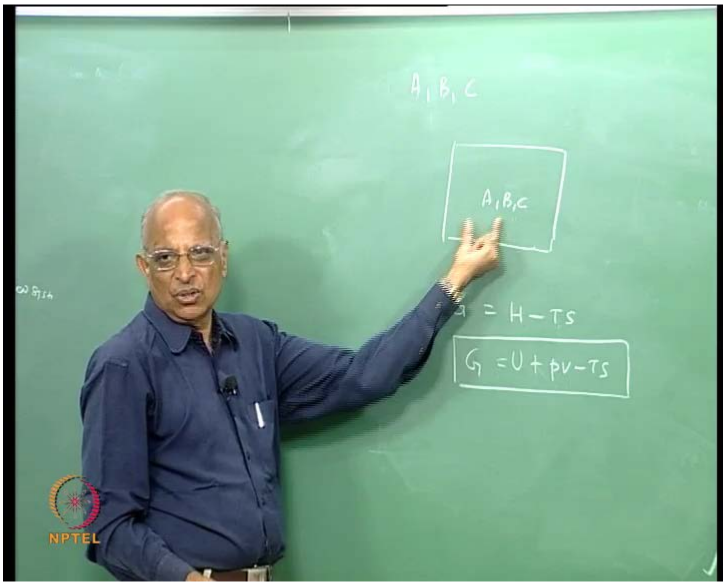

This is equal to enthalpy minus P s. That means when the temperature of the system is same as the surroundings, I say gifts free energy g is equal to h minus t s t as defines the non available portion of the work and h is the enthalpy or rather I can write it as U plus PV minus TS is gifts free energy. This gifts free energy tells me the conditions under which the system can do work. That means I took heat, I subtracted the non available part of heat which is not available as work and this is the available part of the work. Therefore, gifts free energy tells me what the work is and what is possible from a particular system.

Therefore, now I look at d G because I still want to relate it to what are the specious which are formed. Therefore, now I take a differential of that and therefore, now I can write d G is equal to d u plus p d v plus V d p plus s d T no minus s d T minus t d s. All what I am looking at is what is the change in gifts free energy. Let us first consider a single specious system for a single specious system I define like this and therefore, I write d G is equal to change in internal energy, u change in d of PV which is p d v plus V d p change in the value of minus s d which is equal to s d T.

Now, you know let us go back to our definition. Supposing, I have a system. The heat which comes into the system d q is positive. The work is done by the system d w is possible and therefore, we always told ourselves that based on this heat is entering work is living, we told ourselves the change d u is equal to d q minus d w.

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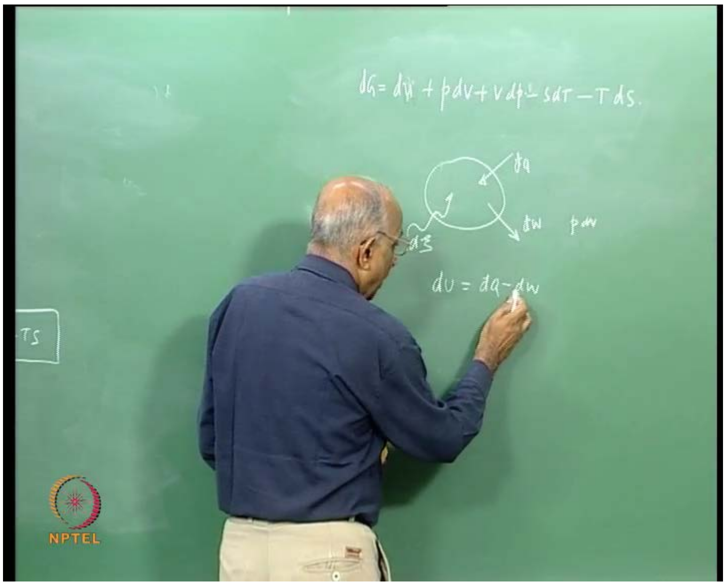

This is for any system. This is valid because some heat is entering d q. Some work is being done d w and the change associated with this. This is the change in the internal energy. Now, you know chemical reactions. Supposing, I have different specious here cannot do d w which is the p d v work, rather if I were to do some other work on this system let us say, d d zeta which is not p d v work, but the work associated with let us say, gases interacting with each other or so. I can now write minus d w plus d zeta.

Therefore, let me take that d w and plug it into the earlier equation. What is it I will get? Now, I get d G is equal to that is the change in gifts free energy is equal to d u plus p d v plus V d p. Now, minus T d s minus s d T I have just copied it out. Let us now take the value of d u. D u is equal to I get d q. What is d q? That is we are having temperature and the change is the value. This is how d q by t depend as d s. Therefore, I can write here, I write as equal to T d s minus d w p d v plus the non p d v type of work. Now, I get T d s cancels p d v cancels and now, I get d G is equal to V d p minus s d T plus the non p d v type of work associated with the gases.

Now, I tell myself I am considering a constant pressure system and a constant temperature system because I want to find out what is the equilibrium state of the system at a given temperature pressure. What are the numbers of moles of gases which can exist? Therefore, my d p is 0 by d t is 0 and therefore, d G is equal to d after work. Therefore, when I say d G is 0, all what I mean is there is no question of any inherent work in the system or rather if there is no work which is being done on the system. That means d zeta is equal to 0 will be a state of equilibrium.

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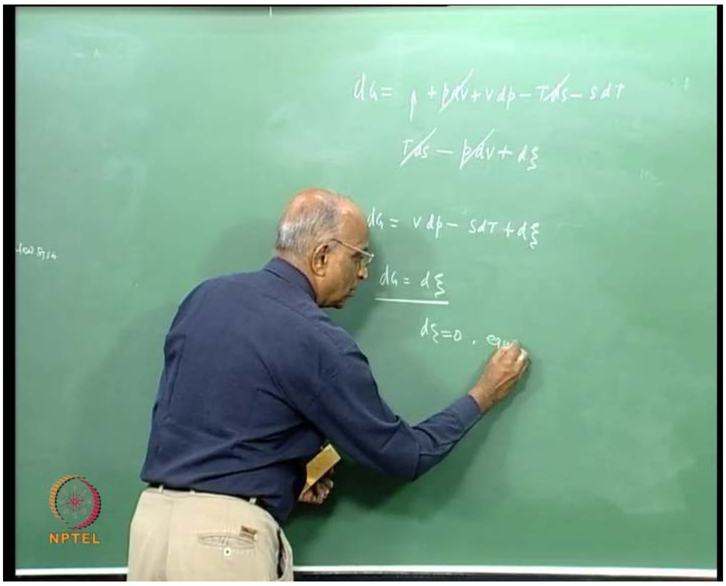

When can I affect a system? If I do some work on the system, I am disturbing the system. Now, the work, external work which I am doing on the system is 0. Therefore, d zeta is 0 and therefore, d G is equal to 0 defines equilibrium. Is it not?

Therefore, now I can write in a simple way. For a gas I can write d G is equal to V d p minus s d T plus which is external to the system. I tell myself at constant pressure and temperature d G tells with the equilibrium because if I do work on the system, some positively v g increases. If the system does work on the outside, d G is negative and d G decreases whereas, d G is negative. Therefore, d G decreases or if d zeta is 0, no work being done. This is equilibrium which becomes equal to 0.

Now, I consider c b is not interested in a single component gas. We are interested in a mixture of gases and therefore, how do I formulate this problem when I have a number of gases, different gases. Let us say one gas here, one gas here. I want to find out the equilibrium situation of all these gases together. If now I tell myself well, I have defined g only for a system of a single gas and I want to define for a mixture of gases. Therefore, I say if I have now I can tell myself g is equal to or let me yeah g is equal to in addition to whatever I write as equal to h or let us put it as u plus PV minus t s.

Now, this is for a single component gas. If I have a large number of gases, I can write this as equal to d G by I vary one mole of a gas n 1. That means I have gas n 1. I put one more mole on this keeping all other moles constant at the same pressure and temperature, such that I do not change any of these values and then, I multiply by d n 1 such that I say d n j where j is not is I do not change. Let us say, a d d n I this is here I say n j with j naught equal to the value of I over here.

I think I have to qualify this in a better way. Let me see what it is. I am trying to say if I have a single component gas, I say g is equal to u plus PV minus t s. Now, all what I am saying is when I add something more over here, something more because I am adding some more gases and changing the value of the gifts free energy and therefore, I say I have a term like d G by d n I coming.

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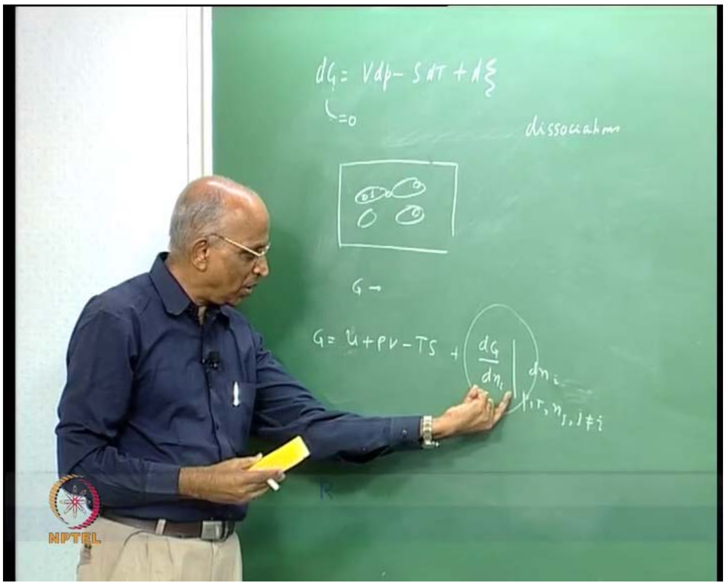

What I will do in the next class is I will use such relations and the equilibrium condition to be able to determine how we can find out the number of moles of different gases, which can exist in equilibrium. That is what we say is the case when I consider dissociation is taking place. May be I will complete it in the next class, but I will introduce a terminology known as chemical potential. We will go through this again in the next class.

Well, thank you then.