Rocket Propulsion

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Module No. # 01
Lecture No. # 19

Shifting Equilibrium and Frozen Flow in Nozzles

Good morning, in the last few classes we have been talking of chemical propellants.

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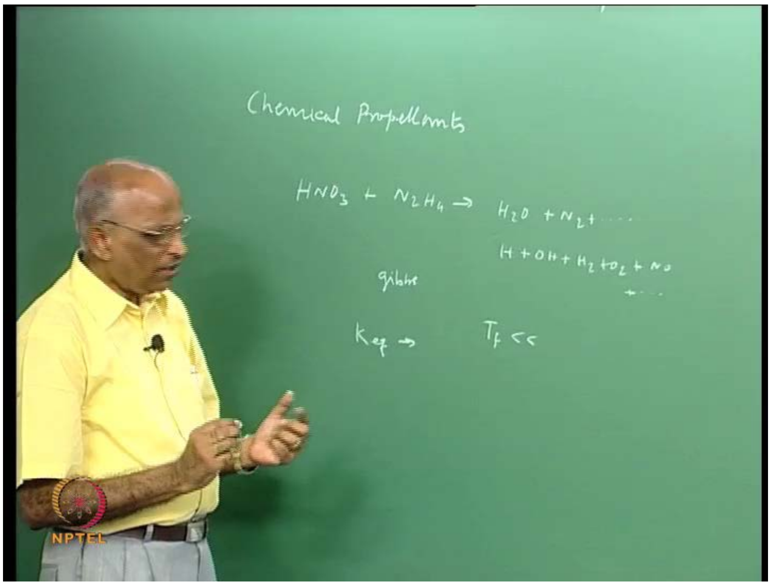

We have been trying to find out what are the characteristics which we must look for in chemical propellants. While doing this, what is it we have done so far let us take a quick let us take a stock of what we have done so far. Suppose, I have propellant like let us say HNO_3 we said it is an oxidizer because it consists more of oxygen than a fuel. And then I react it with something like a hydrogen which we say is a fuel, maybe we get products and these products could be H_2O could be something like N_2 could be something like this.

This all this is the completed product of combustion, but if the temperature we said is high this could be dissociate into let us say HOH may be H_2 could also, come may be O_2

could also, come N could combine we could get NO and so on we could get a number of specious. Therefore, to be able to find out the products and there moles in the products that means, the concentration of the different specious in the product, we define something known as gifts free energy. And for a given temperature which would be the flame temperature at the given pressure we said all these things will be in equilibrium and that is what we were trying to do.

For this we also, went ahead and defined something known as K equilibrium, which tells us the condition that means, the product of the pressures of each of these specious are in equilibrium and we defined this as K equilibrium. And using K equilibrium we were trying to find out what will be the products and mind you this is dissociation or the numbers of specious are important. Because the energy liberated in a reaction depends on the total heat of formation of the products minus the total heat of formation of the reactance with a negative sign. And if I have dissociated specious I may not get that much of energy and my flame temperature or the adiabatic temperature may be smaller.

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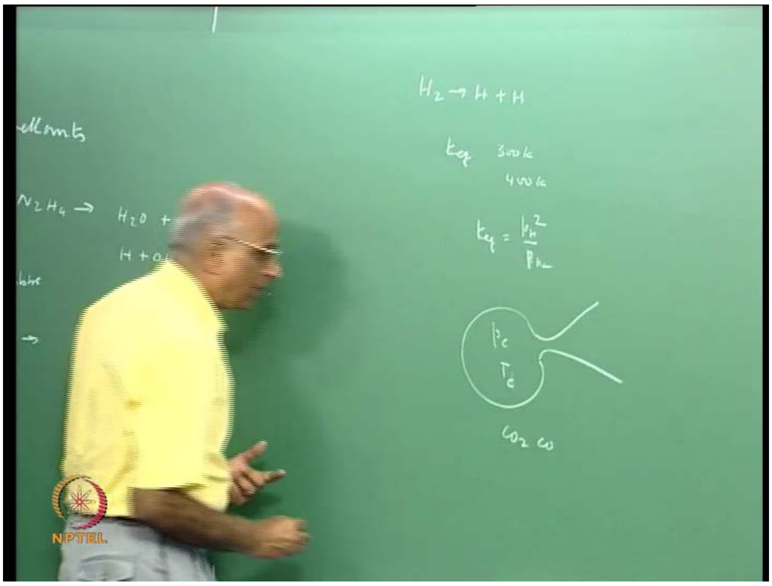

Therefore, this is important and that is why we were bit trying to calculate and the illustrated this with the result for H2 going to H plus H. And we use the gifts free energy what was given we could calculate the value of K equilibrium at two temperatures of we calculated at let us say 300 Kelvin. And we calculated at 4000 Kelvin and we found out may be at higher temperature we get more of H. Because the K equilibrium value was higher and we were able to write out let us say K equilibrium is equal to p H square that is the partial pressure of hydrogen square to p H2. Partial pressure of hydrogen and based on the value we could calculate the proportion of this and the partial pressure.

This is all we have been doing so far, but why did we say these things are important? This is important because in any chamber let us say I have a rocket chamber like this and at the exit of the chamber I have the nozzle, which is expanding the products of combustion. This is at a pressure let us say p C, which is quite high let us say may be 220 MP a or may be 200 bar 300 bar or so. I can always calculate the flame temperature which we called as the combustion temperature. To be able to calculate the combustion temperature I need to know precisely what is the products of combustion? We decided earlier, we said well if it is storchiometric I will have completed combustion products and I can calculate the value of q.

Once I know the value of q I know the specific heat distribution and therefore, I can calculate the temperature. I can also, calculate the phase changes the temperature change from the initial value to the boiling point at that phase change and again boiling temperature to flame temperature for each of the cases. Therefore, we know how to calculate this for storchiometric? When we said fuel rich we made an assumption saying that if it is fuel rich first the nitrogen gets nitrogen in the fuel gets converted to N2 in the products and it does not really give any heat. Then the hydrogen gets attack by the oxygen and we get H2O. And then the balance goes to react with carbon and this is how we did? And it was an approximate way of finding out what is the value of CO2 what is the value of CO?

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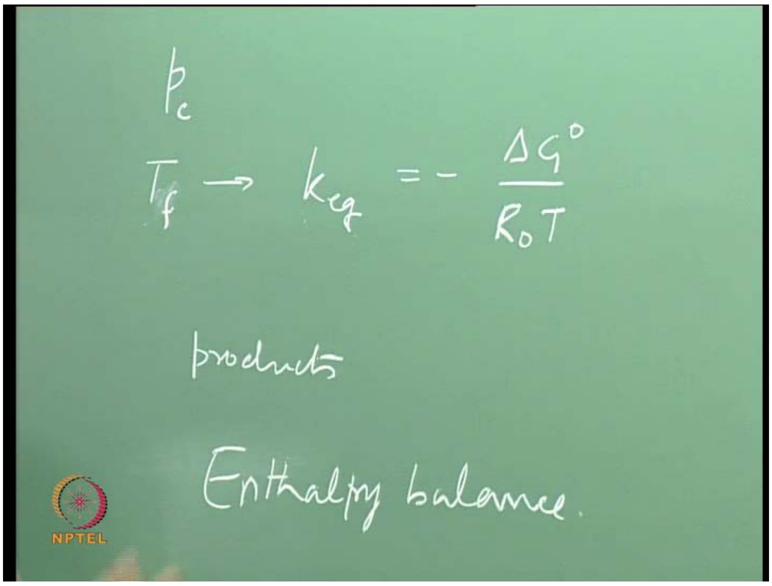

p_c

$T_f \rightarrow k_{eq} = -\frac{\Delta G^\circ}{R_0 T}$

products

Enthalpy balance.

But then if I can do the same problem by assuming let us say that the products of combustion are at a pressure p. And if I know assume that the product of combustion is at a temperature T f at a pressure T C. And then I go ahead for each of the specious or a combination of specious I put some chemical reactions find out the value of K equilibrium, which we said is equal to minus delta into gifts free energy for the reaction divided by R naught universal gas constant into the particular temperature. Gifts free energy at this temperature at the assume temperature T at the flame temperature I can calculate K equilibrium. And using this K equilibrium I can know calculate my products.

And now, I calculate the products, but I know that I have assumed this temperature therefore, I have to check whether this temperature is true therefore, I do the enthalpy balance. (No audio from 05:59 to 06:07) What is the enthalpy balance? My heat of formation of the products must minus the heat of formation of the reactance with a negative sign must be the energetics of the propellant, which divided by the C p must give me back this temperature. If it does not give me well my assumed value is wrong and I must do it. Let me illustrate this through an example, with which we had got started in the last class let us do this particular one.

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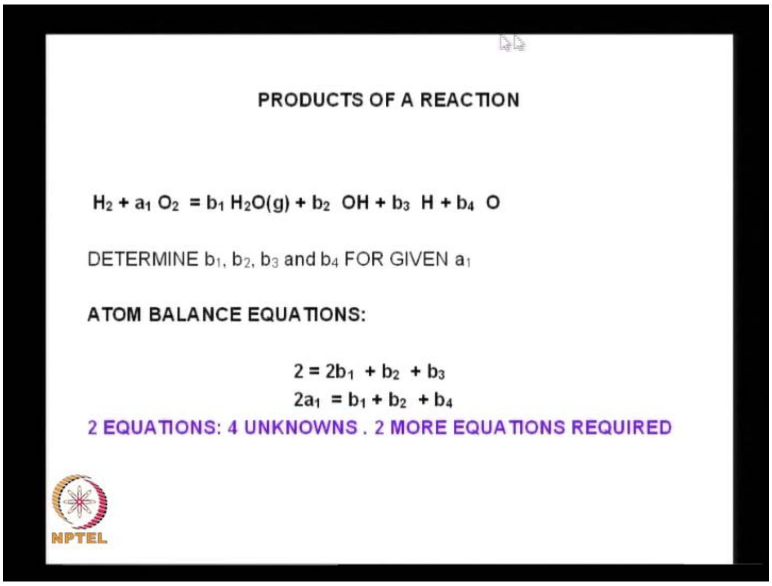

PRODUCTS OF A REACTION

$H_2 + a_1 O_2 = b_1 H_2O(g) + b_2\ OH + b_3\ H + b_4\ O$

DETERMINE b_1, b_2, b_3 and b_4 FOR GIVEN a_1

ATOM BALANCE EQUATIONS:

$$2 = 2b_1 + b_2 + b_3$$
$$2a_1 = b_1 + b_2 + b_4$$

2 EQUATIONS: 4 UNKNOWNS . 2 MORE EQUATIONS REQUIRED

We in this particular reaction or the reactance what I take is hydrogen with a 1 moles of oxygen. Now, I this the reaction between hydrogen and a 1 moles of oxygen gives me d 1 moles of steam in the gas phase b 2 as hydroxyl radical b 3 as H atom and b 4 as O atom. I just assume it is true, you could have assume something else this is just to illustrate how we calculate? The products of a reaction and us the products of a reaction how I go ahead and calculate the flame temperature this what I want to illustrate. Therefore, what is it I first have to do? I must calculate the value of b 1 b 2 b 3 and b 4 if I know this I can calculate the heat of formation of the products, which are formed I know the heat of reactance of this and I subtract this and this with a negative sign that will mean my heat of combustion.

If I know the specific heat of each of these constituents multiplied by the moles, which if I use the molar specific heat I can get the temperature this is what I want to do. Therefore, to do this I first need to know what must be my value of a 1 how do I get a 1? Mixture ratio is specified mixture ratio is mass of oxidizer to mass of fuel and we saw in the last class. That the mixture ratio for a reaction such as involving H2 plus a 1 O2 the mass of oxygen is 32 into a 1 divided by 2, which is 16 a 1 16 a 1 is mixture ratio and if the mixture ratio is specified, let us say mixture ratio of we said must generally be fuel rich.

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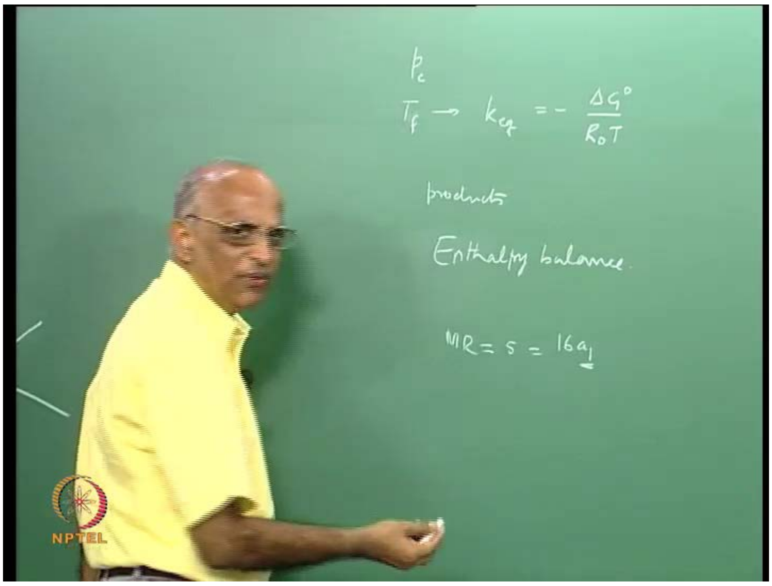

Let us say storchiometric mixture ratio for hydrogen oxygen is 8. Let us say 5 therefore, this is equal to I get 16 a 1 is the value I can get the value of a 1. Whatever, be the mixture ratio I can do this problem. Now, to be able to get b 1 b 2 I must be able to get the atoms on the left hand side to be equal to the atoms on the right hand side. And therefore, I say I have two atoms of hydrogen, which on the right hand side I get two b 1 plus 1 atom here b 2 plus 1 atom here b 3 this is the atom balance equation for h.

Similarly, for O I have two a 1 on the reactance side and I have 1 O b 1 plus 1 O b 2 plus 1 O b 4. Therefore, I know I get two equations which that which connects the moles of my products which I have assumed to be b 1 b 2 b 3 b 4. And which I want to determine for a given value of a one and therefore, I get these two equations. But then I find a 1 is known we just say for a mixture ratio of 5 a 1 is 5 by 16 and therefore, now I need to know what is going to be my value of b 1 b 2 b 3 b 4.

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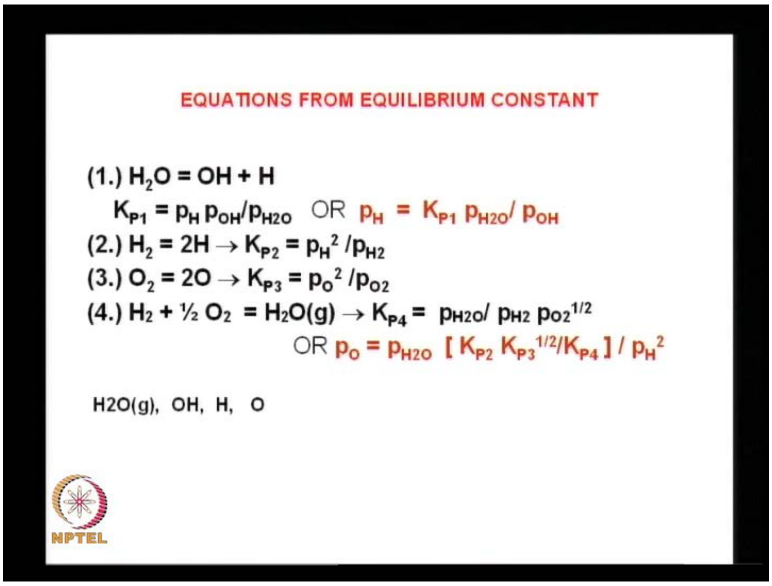

EQUATIONS FROM EQUILIBRIUM CONSTANT

(1.) $H_2O = OH + H$

$K_{P1} = p_H\, p_{OH}/p_{H2O}$ OR $p_H = K_{P1}\, p_{H2O}/\, p_{OH}$

(2.) $H_2 = 2H \rightarrow K_{P2} = p_H{}^2\, /p_{H2}$

(3.) $O_2 = 2O \rightarrow K_{P3} = p_O{}^2\, /p_{O2}$

(4.) $H_2 + \frac{1}{2}\, O_2 = H_2O(g) \rightarrow K_{P4} = p_{H2O}/\, p_{H2}\, p_{O2}{}^{1/2}$

OR $p_O = p_{H2O}\, [\, K_{P2}\, K_{P3}{}^{1/2}/K_{P4}\,]\, /\, p_H{}^2$

H2O(g), OH, H, O

I have 4 unknowns, but one two equations and therefore, I need two more equations and to use to get the next two equations. I use the value of the equilibrium constants and how do I do use it? Then let us say I have I assume well H2O could have dissociate with 2 OH and OH. If this is case then the value of equilibrium constant for this reaction is equal to partial pressure of OH into partial pressure of H divided by partial pressure of H2O. We said we could express either as a concentration which is K C in terms of (( )), but for (( )) we said let us use partial pressure itself.

Or rather from this equation I get p H, which is from the right hand side I take it over here is equal to K p 1 into p H2O divided by p OH. I know the now the value of p H in terms of p H2O and p O h. Similarly, I would also like to get the partial pressure of oxygen and for that I use I write the following three equations. H2 could have got dissociated to 2H O2 could have got dissociated to T u 2 O. For this particular reaction H2 could 2 H I get K p 2 is equal to p H square divided by that means, I had p H into p H p H square divided by p H2 O 2 going to 2 O I can write the reaction rate constant for this cycle as equilibrium constant I call as K p 3 and K p 3 is equal to p O square divided by p O2 over here.

I have one more equation, I said well I can also consider H2 plus half O2 is equal to H2OG that is gas phase and therefore, for this reaction I say the equilibrium constant is K p 4. And K p 4 is equal to partial pressure of H2O over here, divided by p H2 and half

O2 means p O2 half. Therefore, I look at these three equations and from this equation I get the value of may be p H2 is equal to K p 2 by p H square. I get the value of O2 is equal to K p 3 by p O square. I substitute it in this particular equation and I get p O is equal to I get the value of p H2O into K p 2 K p 3 half divided by K p 4 into p H square.

How did this come? Let us take a look I have p H square here p H2 is equal to K p 2 by p H square similarly, I have in this case p O2 from this reaction p O2 half is equal to K p 3 to the power half divided by p O I substitute it. And I get p O it I i bring p O to the left side I get partial pressure of oxygen is equal to partial pressure of steam into K p 2 K p 3 to the power half divided by K p 4 divided by p H square. Now, what is it I have done? See let us again take stock of why we are doing all these? What is it we said? In the products we have H2O OH H and O that means, we have 4 specious and now, out of these four specious.

What is it we have done? We have expressed p O in terms of p H square and p H2O that is p H and p H2O. And also p H in terms of H2O and H in other words, I take two of the partial pressures of two specious express it in terms of partial pressure of two other specious. Essentially therefore, we have we got four specious. What were the four specious? b 1 of H2O let us put it again b 1 of H2O b 2 of OH b 3 of H and b 4 of O now, we are able to relay two of them to the remaining two of them and therefore, now I can close my equation because I have two more equations.

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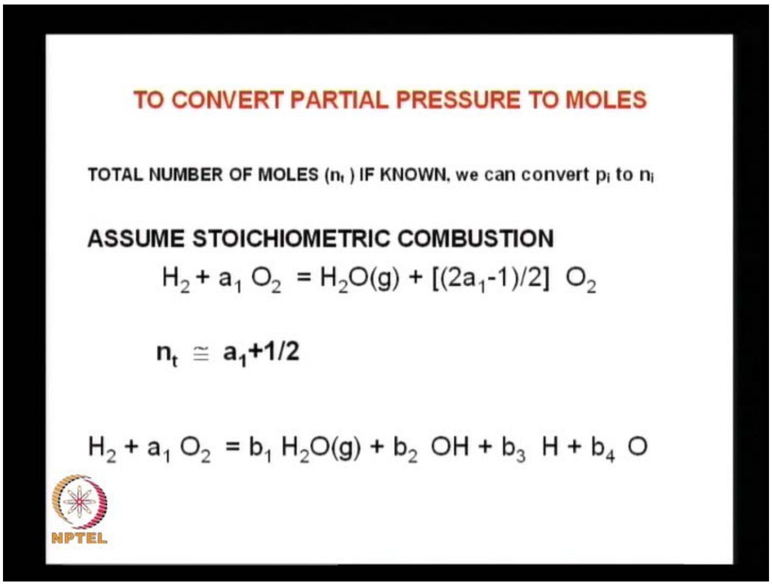

TO CONVERT PARTIAL PRESSURE TO MOLES

TOTAL NUMBER OF MOLES (n_t) IF KNOWN, we can convert p_i to n_i

ASSUME STOICHIOMETRIC COMBUSTION

$$H_2 + a_1\, O_2 = H_2O(g) + [(2a_1-1)/2]\ O_2$$

$$n_t \cong a_1 + 1/2$$

$$H_2 + a_1\, O_2 = b_1\, H_2O(g) + b_2\, OH + b_3\, H + b_4\, O$$

And therefore, let us put it together again that four, but before I put partial pressure my equations are in terms of b 1 b 2 b 3 b 4 and what I have determined is partial pressure of H2OG partial pressure of OH partial pressure of H and partial pressure of O. Now, how do I convert partial pressure to b 1? I think that something which is important let us just do it on the board.

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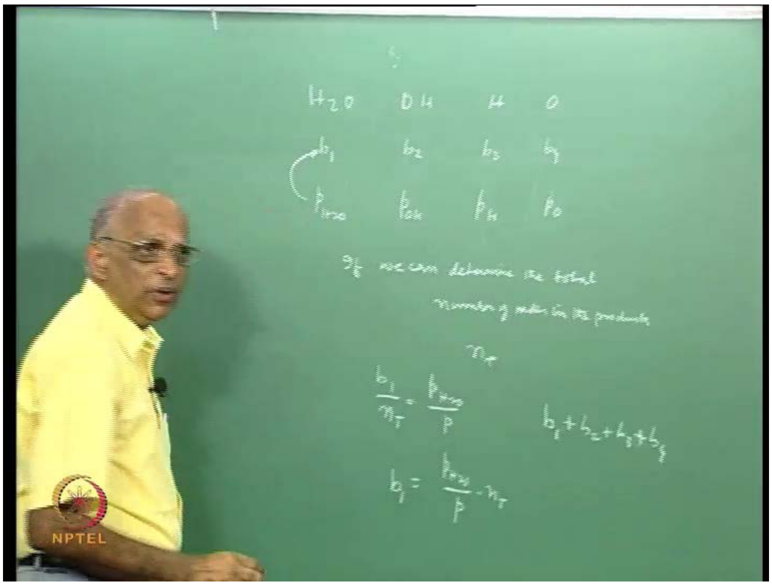

Let me again repeat what I am telling that? I have H2O I have OH I have H I have O and according to the equation what I have? I have b 1 moles of this I have b 2 moles of OH I have b 3 moles of H and I have b 4 moles of O. Now, what is it I did through equilibrium constant? I say the partial pressure of H2O is so much the partial pressure of OH is so much the partial pressure of H is so much the partial pressure of O atom is in this. Now, I have the atom balance equation in terms of b 1 b 2 b 3 b 4, but I have equilibrium relations, which gave me in terms of partial pressure how do I convert p in terms of b one.

To be able to do that, if I can find out if we can determine the total number of moles in the products, then I can always go back and determine this how do I say? Let us say that the total numbers of moles in the product are let us say N T total number. And now the total number of moles of O a of H2O is b 1 therefore, b 1 by total number of moles is equal to I can now write this is equal to partial pressure of hydrogen divided by the total pressure in the chamber. And therefore, I get b 1 as equal to p partial pressure of water divided by hot steam divided by the total pressure multiplied by the total number of moles.

Therefore, if I can determine the total number of moles it will be possible for me convert. The partial pressure of each of these specious into their respective number of moles is it. Now, to do that you know I cannot know I all I know is the total number of moles in the products, according to this relation is b 1 let me put it at the side over here b 1 plus b 2 plus b 3 plus b 4 over here. But I still do not know the value of b 1 therefore, the total number of moles are not known. Therefore, we make an assumption and the assumptions made is you know let us assume that the reaction is storchiometric. And based on this if we keep working with this we find that the total number of products, which we form is not very different from the storchiometric.

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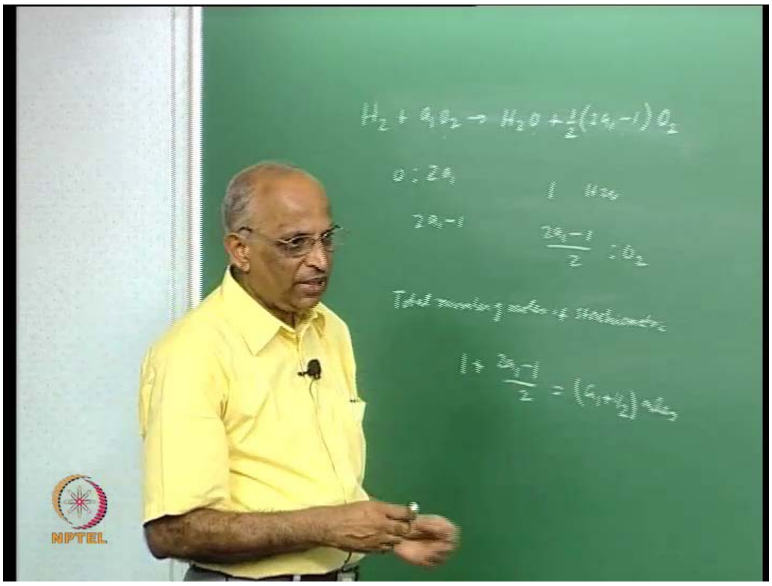

Let us say let us take that same reaction again we said H2 plus a 1 O2 if it is storchiometric combustion complete products of combustion would have been formed. Therefore, I would have got H2O plus now, what is it I had two of a 1 O had two of a 1 I have consumed one I am left with 2 a 1 minus 1. Therefore, the amount of oxygen left in this reaction as per this relation should be plus I have 2 a 1 minus 1 of O, but I would like to put it in terms of O2, which is left that should I get half over here. If I were to assume that this reaction is storchiometric I get one mole of H2O and I get the balance that is 2 a 1 minus 1, which is (( )) depleted here divided by 2 is what is left I have therefore, 2 a 1 minus 1 divided by 2 two of oxygen which is left.

Therefore, the total number of products which are formed or total number of moles of products, according to this reaction if storchiometric is going to be one plus I get 2 a 1 minus 1 divided by 2, which is equal to I get now a 1 plus half total number in the products. Mind you this assumes storchiometric, but the general thinking is or generally, if you do as number of problems the number of moles are not very much different, but then we will go back and correct it as we go along as I will show you.

Therefore, to begin with we will assume that the total number of moles what we are going to get is going to be a 1 plus half mind you it is storchiometric I am assuming let the total number of moles in the products be this. If this is so I know now, the total number of moles over here and therefore, I can calculate p H2O as equal to b 1 into p divided by N T. And therefore, I do that next and what is that I get? b 1 is equal to let us go back here b 1 is equal to p H2O divided by the pressure into the total number of moles or therefore, I can get the value of b 1.

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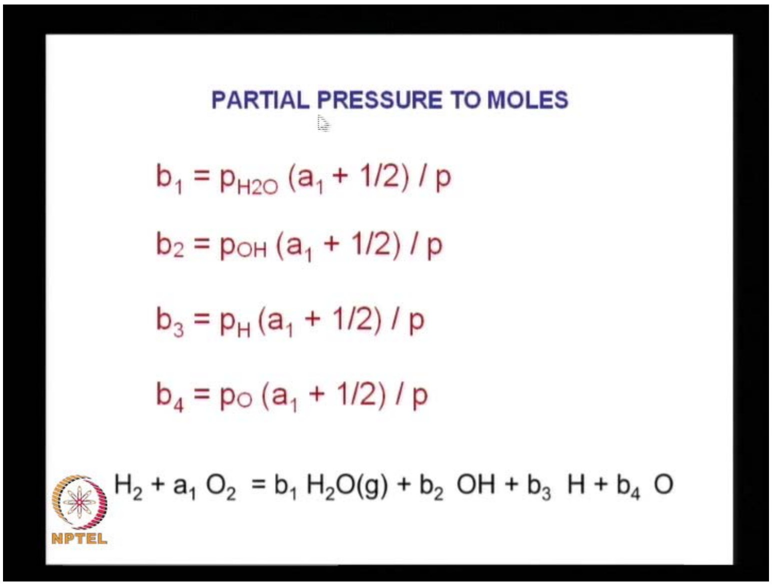

PARTIAL PRESSURE TO MOLES

$b_1 = p_{H2O} (a_1 + 1/2) / p$

$b_2 = p_{OH} (a_1 + 1/2) / p$

$b_3 = p_H (a_1 + 1/2) / p$

$b_4 = p_O (a_1 + 1/2) / p$

$H_2 + a_1 O_2 = b_1 H_2O(g) + b_2 OH + b_3 H + b_4 O$

Similarly I get the value of b 2 over here as the partial pressure of oxygen into the total number divided by the total pressure b 3 in terms of p H into the total number of moles divided by the total pressure and b 4 partial pressure of oxygen atom into total number of moles divided by the pressure. And what is it we have done? We have converted partial pressure of H2OG partial pressure of OH partial pressure of H partial pressure of O into b 1 b 2 b 3 and b 4.

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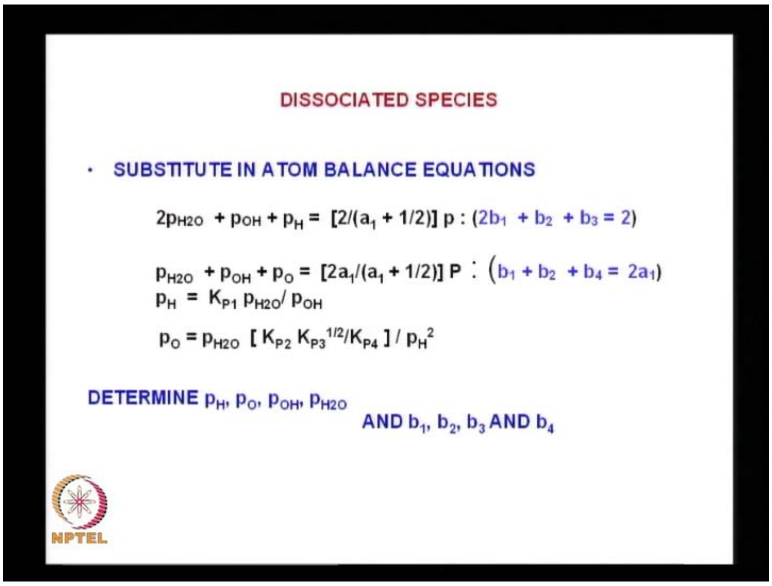

DISSOCIATED SPECIES

- SUBSTITUTE IN ATOM BALANCE EQUATIONS

$2p_{H2O} + p_{OH} + p_H = [2/(a_1 + 1/2)]\, p : (2b_1 + b_2 + b_3 = 2)$

$p_{H2O} + p_{OH} + p_O = [2a_1/(a_1 + 1/2)]\, P : (b_1 + b_2 + b_4 = 2a_1)$

$p_H = K_{P1}\, p_{H2O}/ p_{OH}$

$p_O = p_{H2O}\, [K_{P2}\, K_{P3}^{1/2}/K_{P4}] / p_H^2$

DETERMINE $p_H, p_O, p_{OH}, p_{H2O}$ AND b_1, b_2, b_3 AND b_4

But we already had the relation between b 1 b 2 b 3 b 4 and what was the relation we had from atom balance? We had 2 b 1 plus b 2 plus b 3 is equal to 2 we also, had b 1 plus b 2 plus b 4 was equal to 2 a 1 H2O. Therefore, we can use these two relations and we can now, substitute for b 1 b 2 b 3 in terms of the partial pressures and we get 2 p H2O plus p OH plus p H divided by this particular one that is we had to divide this to get p this I bring it on this side and I get 2 a 1 into this one. I think this should have been one here and this should have been 2 a 1 therefore, this is one here. And similarly, I get from this relation p H2O plus p OH plus p O is equal to the value of 2 a 1 divided by a 1 plus half into the value of p over here.

That means, we have succeeded in putting the atom balance equations which were in moles in terms of the partial pressure of H2O OH h and p O. Mind you we also, had two other relations then we had the relations for p H in terms of p H2O p OH through the equilibrium constant and we derived the relation for p O in terms of p H2O and p H square. Therefore, we have four equations in four unknowns. And what are the four unknowns? Partial pressure of H2OG, partial pressure of OH, partial pressure of H and partial pressure we can solve this equation and determine the value of p H p O p OH and p H2O. Mind you the equations are not that linear or not, but we can always use some scheme like the Newton (( )) scheme or some scheme to be able to solve this and it can be solved very easily.

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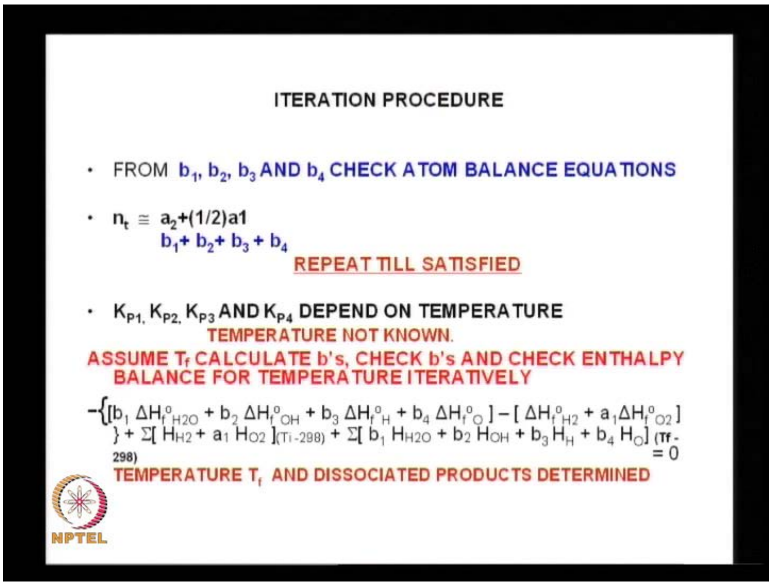

ITERATION PROCEDURE

- FROM b_1, b_2, b_3 AND b_4 CHECK ATOM BALANCE EQUATIONS
- $n_t \equiv a_2+(1/2)a1$
  $b_1+ b_2+ b_3 + b_4$
  REPEAT TILL SATISFIED
- K_{P1}, K_{P2}, K_{P3} AND K_{P4} DEPEND ON TEMPERATURE
  TEMPERATURE NOT KNOWN.

ASSUME T_f CALCULATE b's, CHECK b's AND CHECK ENTHALPY BALANCE FOR TEMPERATURE ITERATIVELY

$$-\{[b_1\, \Delta H^o_{f\,H2O} + b_2\, \Delta H^o_{f\,OH} + b_3\, \Delta H^o_{f\,H} + b_4\, \Delta H^o_{f\,O}] - [\Delta H^o_{f\,H2} + a_1 \Delta H^o_{f\,O2}]\} + \Sigma[H_{H2} + a_1 H_{O2}]_{(Ti-298)} + \Sigma[b_1 H_{H2O} + b_2 H_{OH} + b_3 H_H + b_4 H_O]_{(Tf-298)} = 0$$

TEMPERATURE T_f AND DISSOCIATED PRODUCTS DETERMINED

Once we determine the value of p H I must go back and determine the value of b 1 b 2 b 3 b 4. What I do? I go back substitute it again in the equations for b 1 b 2 b 3 b 4, which we had here b 1 similarly, b 2 b 3 and now I get the values of b 1 b 2 b 3 b 4. That means, I know the number of moles of H2OG I know the number of moles of OH I know the number of moles of H I know the number of moles b 4 of O over here. Now, that means I am I know all this, but now I have assume what was my assumption end? The total number of moles was equal to a 2 plus half a 1 rather this should have been what we had was a 2 was one we had 1 plus half into a 1.

And therefore, this was known to me, but I assumed this, but actual number of moles in the products is b 1 plus b 2 plus b 3 plus b four. If this is going to be different from this well I assume this to be the total number of moles redo the calculations till b 1 b 2 b 3 b 4 converges and that will be my final value of b 1. That is number of moles of H2O number of moles of OH number of moles of H and number of moles of O.

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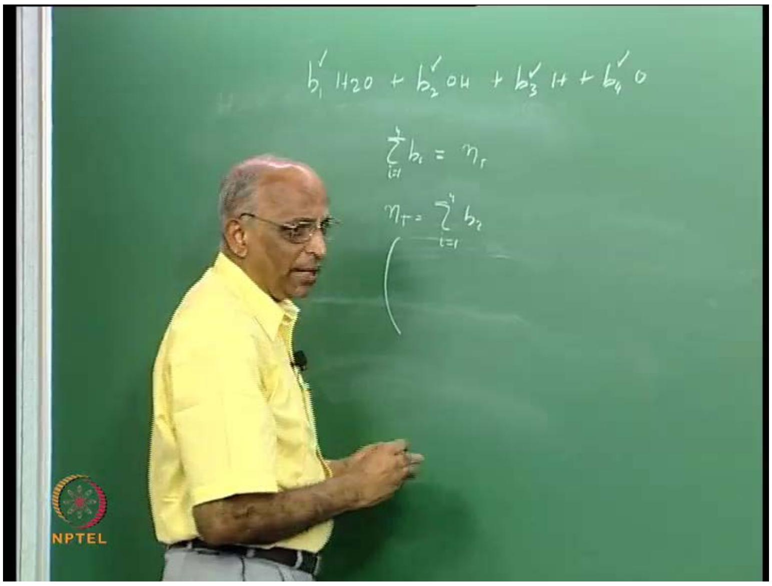

In other words what is it we are going to do? What is it we have done or what is it we need to understand in this? We need to know b 1 H2O we need to know b 2 how much of OH we need to know how much of may be H and the how much how many moles of O are there. To be able to do that we assume the total number of moles to be storchiometric and then we determine b 1 b 2 b 3 b 4. Then we said summation of b I as I goes from 1 to 4 must be must be the same as total number of moles, which we have assumed. If it is no now, let me again assume N2 is equal to summation I is equal to 1 2 4 and take it as the thing. And again repeat the calculation till I get consistent or converged value the same value for b 1 b 2 b 3 b 4 coming.

We go through this look get b 1 b 2 and after I am able to get all these things, to be the same. I go and write out my enthalpy equation again and what is my enthalpy equation? I need to check whether the heat of formation of the products I have b 1 moles of water heat of formation of H2O is known b 2 moles heat of formation of OH is given b 3 moles heat of formation of H is given b 4 moles heat of formation of this is given minus heat of formation of the reactance hydrogen and O one moles of heat of formation of oxygen. Therefore, this is my net heat of reaction at the standard condition and this heat partially goes into supplying. The heat required to change the liquid hydrogen to it is boiling point then the phase change plus the change from the boiling point to the to the standard condition of 298.

Similarly, for oxygen from the liquid state to the boiling state to the latent heat and then the sensible heat or heat of the gas from the boiling temperature to 298 plus for each of the moles, I have something like the specific heat into the number of moles into T f minus 298 is what is given. And this must be satisfied if I have to if my values of b 1 b 1 b 2 b 3 are correct at the temperature which I have assumed. If my assumed temperature is not correct then this will not be equal to 0 I again have to caculate assume a new value of temperature calculate the value of K p 1 K p 2 K p 3 K p 4. At the new temperature again due to the do the enthalpy balance till my final temperature converges and for this convergence I say that is my flame temperature.

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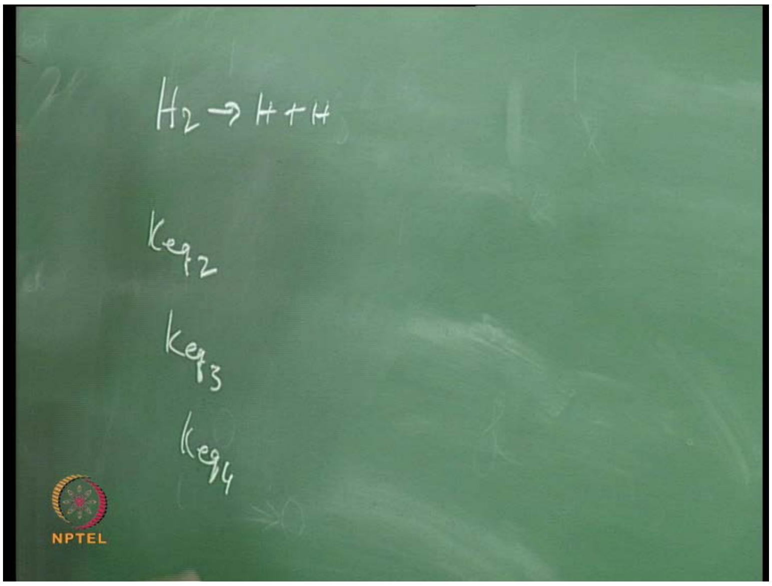

Let me repeat this procedure on the board a little bit with respect to the two convergences. What we are looking for? All what we are telling is that I will have something like K equilibrium for a number of may be four steps we had. We had K equilibrium one for a reaction K equilibrium we said is equal to minus gifts free energy divided by R naught into t. You know to be able to get the equilibrium reaction I need to the value of temperature because K equilibrium is a function of temperature. I have I first assume let the temperature of the reaction be let us say 2000 Kelvin.

Therefore, I evaluate delta G at 2000 for the particular reaction just the same way as we did for the reaction in the last class. H2 is equal to H plus H we evaluated it at 300 we evaluated at 4000. Similarly, I get the value of delta G at the assume value of 2000 I have R naught 8.3 1 4 into 2000 I get the K equilibrium for a reaction. Similarly, I get K equilibrium for reaction two, which I took I take I find the K equilibrium 3 I take a equilibrium 4, which means I have assumed a temperature T f.

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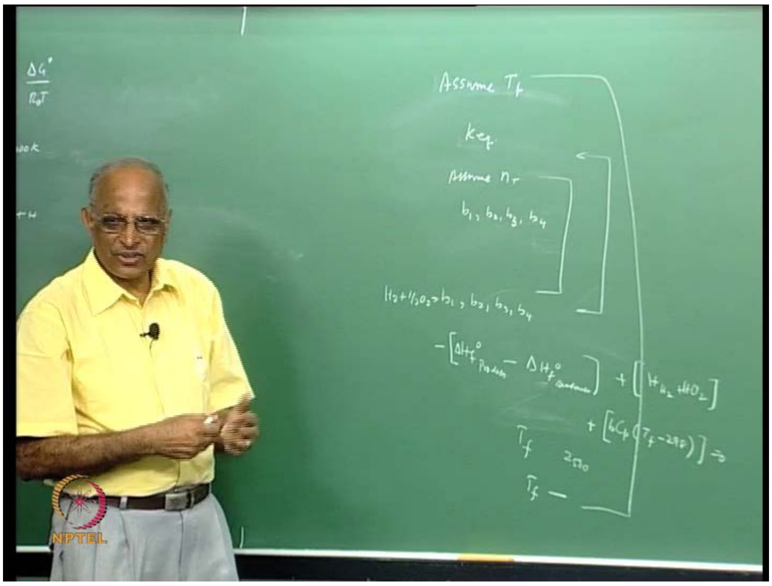

Let us put these two iterations together to being with I assume the value of T f, then I determine the values of K equilibrium. Then once I have written K equilibrium I again assume the value of total number of products, which are available based on storchiometric, then I calculate the value of b 1 b 2 b 3 and b 4. Then I have check whether the assumed value of N T is correct therefore, this must first convert converge and then I get the correct values of b 1 b 2 b 3 and b 4 provided that at this particular temperature. But then I use these b 1 b 2 in the enthalpy balance what is it I do in the enthalpy balance?

In the enthalpy balance I sum up the heat of formation of the total products that means, I multiplied by b I into delta H f I what the products minus I take the net heat of formation of the reactance. And where it is this part of this heat go? It goes into taking we had the reaction H2 plus half O2 it gave me b 1 of the b 1 b 2 b 3 b 4. Therefore, I take the initial state may not be the standard condition part of this heat goes into the enthalpy required to convert the condition of let us say hydrogen from it is original condition to the standard condition. That means, I say I have the liquid phase I have the latent heat phase I have the vapor phase therefore, I have the heat required for H2 that is one of the fuel.

Similarly, I have for the oxygen what is the enthalpy what is required? And again what happens is the balance of heat goes into sensible heat for the products and also, latent heat as applicable for H2O which I do not explicitly write and this must be 0. This goes into this and the and to raise the temperature therefore, I get the new value of temperature now, from this equation that is enthalpy balance. I say I have assumed T f to be 2000 this might give me 2500 and therefore, now I will assume another value of T f which is in between the two. I repeat the process till two successes values give me T f around the same number.

If I am interested in a very tight one may be I say yes it must be 2500 and one or 2500 if I am not interested in such a close one maybe I can put a wider (( )). Which means, I do the problem that means first my convergence is with respect to moles at an assumed value of T f and then I calculate for the value of T f and this is how we do? I like this method of equilibrium constant, because you can see physically what is happening when you are doing it? I will also discuss something about another method which is equally powerful and which is used in many of the course we will discuss it. Therefore, let us let me again repeat this you have b 1 b 2 b 3 b 4 determine set the atom balance equations, again check for the total number of moles repeat till this is satisfied.

But then for this one we had assumed a particular temperature and calculated this, but the temperature was not known then to be able to make sure that this temperature is reasonable or some revision is required. I do the enthalpy balance for the reaction and then find out the final temperature and redo it till T f is known. At this T f I can therefore, calculate the b 1 b 2 b 3 and b 4 which are the correct values of the dissociation specious. Each of us will do for one specific thing using a computer programming and it will help us in a lot of ways we will do something like a project on this.

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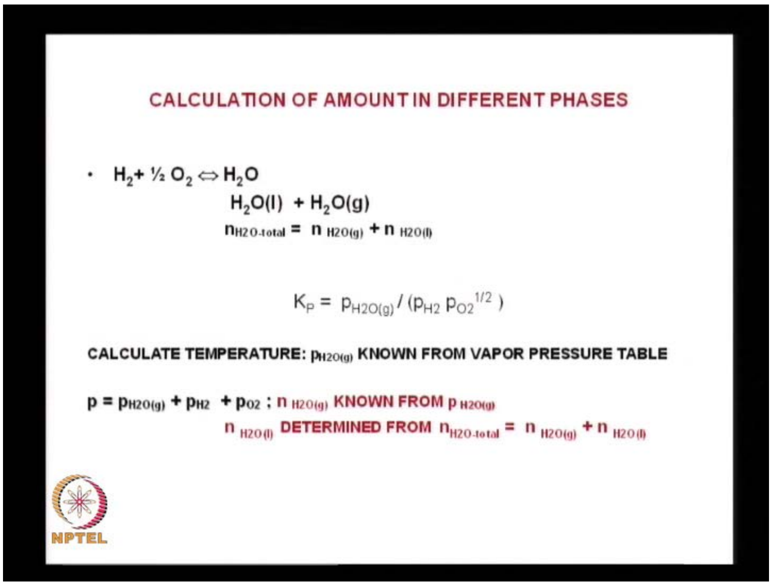

CALCULATION OF AMOUNT IN DIFFERENT PHASES

- $H_2 + \frac{1}{2} O_2 \Leftrightarrow H_2O$

$H_2O(l) + H_2O(g)$

$n_{H2O\text{-}total} = n_{H2O(g)} + n_{H2O(l)}$

$K_p = p_{H2O(g)} / (p_{H2}\, p_{O2}^{1/2})$

CALCULATE TEMPERATURE: $p_{H2O(g)}$ KNOWN FROM VAPOR PRESSURE TABLE

$p = p_{H2O(g)} + p_{H2} + p_{O2}$; $n_{H2O(g)}$ KNOWN FROM $p_{H2O(g)}$

$n_{H2O(l)}$ DETERMINED FROM $n_{H2O\text{-}total} = n_{H2O(g)} + n_{H2O(l)}$

But then you know see it is also, possible that some of the specious what we talked of let us say I have product containing CO2.

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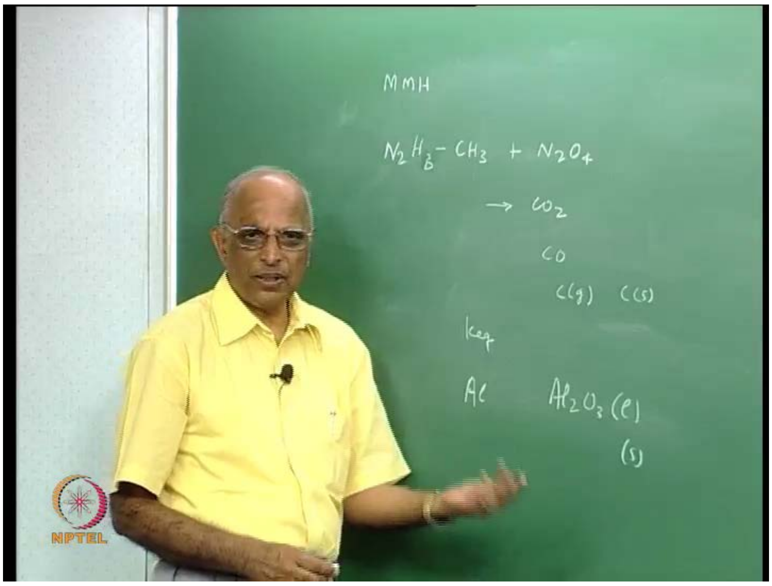

Let us take an example, we considered me mono metal hydrogen I will talk about it in the next class. You have hydrogen N2H4 you take one of the H and substitute it by metal radical this is known as mono metal hydrogen. So, very powerful fuel and it is used in many of the rockets it is a liquid fuel. And if this is going to react with another oxidizer we will consider it in the next class again N2O4. May be my products of combustion could be CO2 if my temperature is very high maybe I could get CO, may be if the temperature is still high maybe I could also get C of the G, but if my temperature is not so high I could also, get some solid form of carbon.

Therefore, how do I distinguish between a gas phase and a solid phase? That also, can be done using equilibrium analysis K equilibrium and this is what I show with respect to water. And let us say liquid phase of H2O which is water and gaseous phase which is steam I take the reaction H2 plus half O2 is equal to H2O. Therefore, I get the total number of moles of water should be the total number of moles in the gas phase by total number of moles in the liquid phase for this reaction I can write K p is equal to p H2OG divided by over here, divided by if it were all gaseous I could have gaseous divided by p H2 by p O2 it need not always be fully gaseous.

But how do I find out the percentage of water? If I can calculate the temperature and in the temperature once I know the temperature the I can always calculate how much of steam will be there? Because steam is saturated at that particular temperature I can get the partial pressure of gas from vapor pressure table. And if I know the amount of what is available I calculate the hydrogen and oxygen I can know the total pressure. And then once I know the proportion of gas from the vapor pressure table I can go back and determine what is the balance of this? And this is how we calculate the proportion of phases?

And this happens you know especially, when we have solid propellant rockets I will consider solid propellants in the next class again. We had lot of aluminum, aluminum forms Al2O3 this Al2O3 could be as a liquid phase could be as a solid phase when it is coming out? And we know all these things have some energy in them. Therefore, we must be able to calculate out and those of you who do a project using solid propellant must be able to differentiate it, but the procedure is extremely extremely something.

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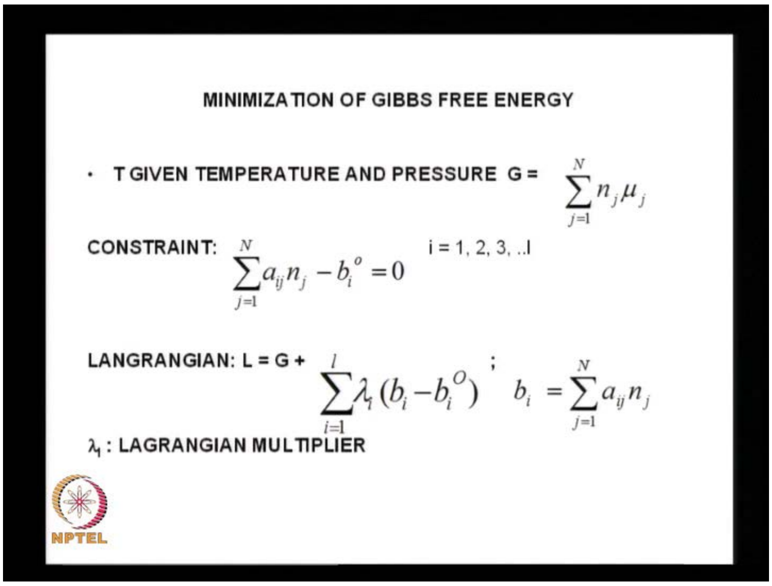

MINIMIZATION OF GIBBS FREE ENERGY

- T GIVEN TEMPERATURE AND PRESSURE G = $\sum_{j=1}^{N} n_j \mu_j$

CONSTRAINT: $\sum_{j=1}^{N} a_{ij} n_j - b_i^o = 0$ i = 1, 2, 3, ..I

LANGRANGIAN: L = G + $\sum_{i=1}^{l} \lambda_i (b_i - b_i^O)$; $b_i = \sum_{j=1}^{N} a_{ij} n_j$

λ_i : LAGRANGIAN MULTIPLIER

This is all about calculation of the specious, but there is also another method which is normally, followed in many of the course whenever you know we deal with rocketry.

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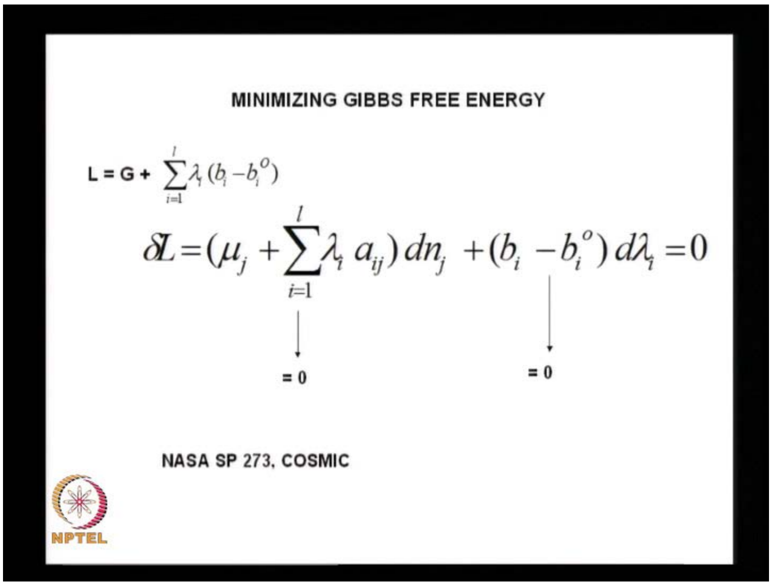

MINIMIZING GIBBS FREE ENERGY

L = G + $\sum_{i=1}^{l} \lambda_i (b_i - b_i^O)$

$$\delta L = \underset{\substack{\downarrow \\ =0}}{(\mu_j + \sum_{i=1}^{l} \lambda_i a_{ij})} dn_j + \underset{\substack{\downarrow \\ =0}}{(b_i - b_i^o)} d\lambda_i = 0$$

NASA SP 273, COSMIC

They say the first thing what we do is yes I use NASA s p 2 7 3 which gives me a computer program this is widely available is available here also. But these has been defined and now we say there is something known as (( )) which is available. It is just the s p 2 7 3 in a more user friendly version what they do is? Instead of going ahead and finding out the equilibrium constants and then finding the temperature what they say is let us say gifts free energy we defined at constant pressure and temperature as equal to N j mu j. And therefore, I can say the total gifts free energy is equal to the let us say in the in our particular case let us write out the value of the gifts free energy what we are going to get for the products. Which we need to determine we have b 1 of H2O we have b 2 of OH we had b 3 of H we had b 4 of O.

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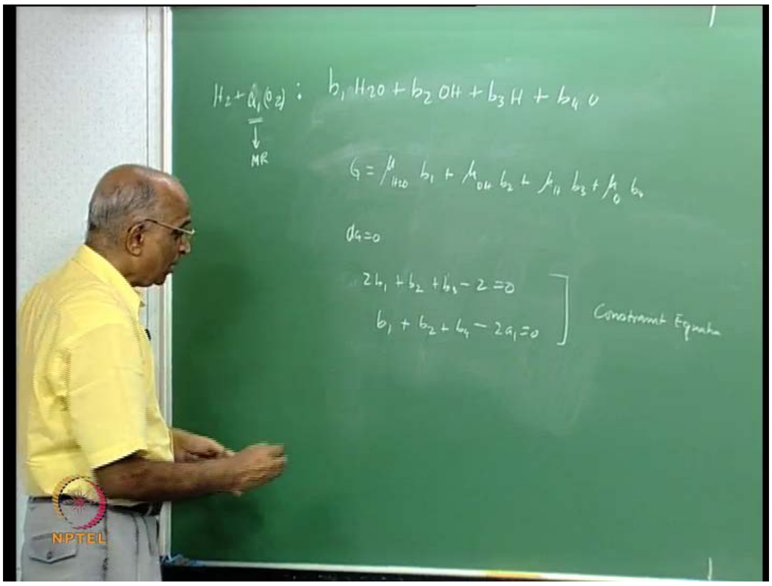

Therefore, the total gifts free energy is equal to mu of H2O into b 1 plus mu of OH into b 2 plus mu of H into b 3 plus mu of O into b 4 this is the total gifts free energy. And what will we said? When gifts free energy is a minimum that is the equilibrium therefore, if I put G as a minimum or rather if I were to put d G as equal to 0 I should be able to find out the value of b 1 b 2 b 3 b 4. And this is a very direct procedure, but it is little involved let us see what is involved in it? But this set of d G equal to 0 must also obey the constraint that the atoms must be conserved and what did we say? Here we had H2 plus half O2 and what were our atom balance equations.

Two is equal to or let us put the right hand side first two b 1 plus b 2 plus b 3 minus 2 equal to 0 and for O balance I had b 1 plus b 2 plus b 4 minus if we had into half of we had a 1 is it not? H2 plus a 1 oxygen this is the this is the reaction it is not half (( )) it is not storchiometric any way. Therefore, I have minus 2 a 1 equal to 0 and this 2 a 1 we determine based on mixture ratio. Therefore, these were the two equations which have to be satisfied because I cannot create atoms in a reaction and therefore, we call this as the constant equation.

Even though I have to minimize the value of gifts free energy d G equal to 0 this must also be obeyed and therefore, we use the method of (( )) multipliers which is what I show here. I define a (( )) l, which I say is equal to l is equal to G plus this is the summation I have two (( )) l is equal to 2 I is equal to one to 2 I wrote this out b 1 minus b prime b I dot b I dot is the left hand side that b I is equal to the storchiometric coefficient into this this was equal to b 1 into H2O plus b 2 into OH and so on.

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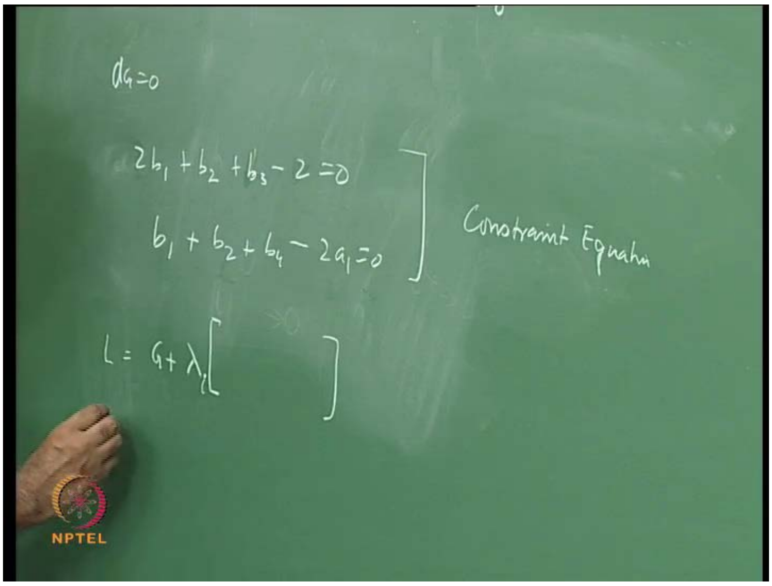

And therefore, this plus this in other words let us put it back again. I should have (( )) I define as equal to G plus lambda into I have this equation coming over here must be ma this is what I define as a (( )) and then I go ahead and tell myself well (( )) is could be 1 and 2 because I have two sets equation. Therefore, lambda I have two of them and therefore, I say d l by d lambda must be 0. And this is the method of what we call as optimization program or optimization or linear optimization G is equal to this plus this.

Therefore, del l is equal to I differentiate over here and I get with respect to N j I get mu j plus summation over lambda I a I j d N j plus the product minus the initial reactant into d lambda i. The in the differentiation of the moles of the products, cannot be 0 the (( )) multiplier is a free multiplier cannot be 0 and therefore, we get this is equal to 0 we get this is equal to 0. We get a set of four equations, which we solve and that gives me the value of b 1 b 2 b 3 b four. May be you all should learn to do both of them I have never really use the (( )) multiplier method, but I when I went through the s p 2 7 3 book I found it is quite simple. I would I personally, like the method of equilibrium constant because I am able to see everything come through in this again we have the four matrices, which we have this matrix involving b 1 b 2 b 3 b 4 which we solve.

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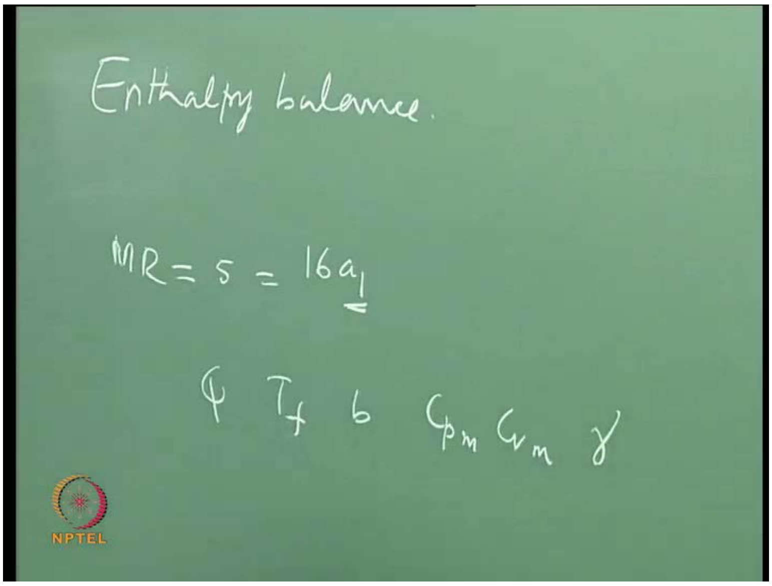

Enthalpy balance.

$MR = 5 = 16 \underline{a_1}$

$\varphi \quad T_f \quad b \quad C_{pm} \quad C_{vm} \quad \gamma$

I think this is how we solve this and we determine the products of combustion? And once the products of combustion you know the heat of reaction you know the C f you once you know the distribution of b. I can find out the value of C p for the mixture I can find out C v for the mixture of the products, I can find out the gamma and I can determine whatever, be the performance I want to determine.

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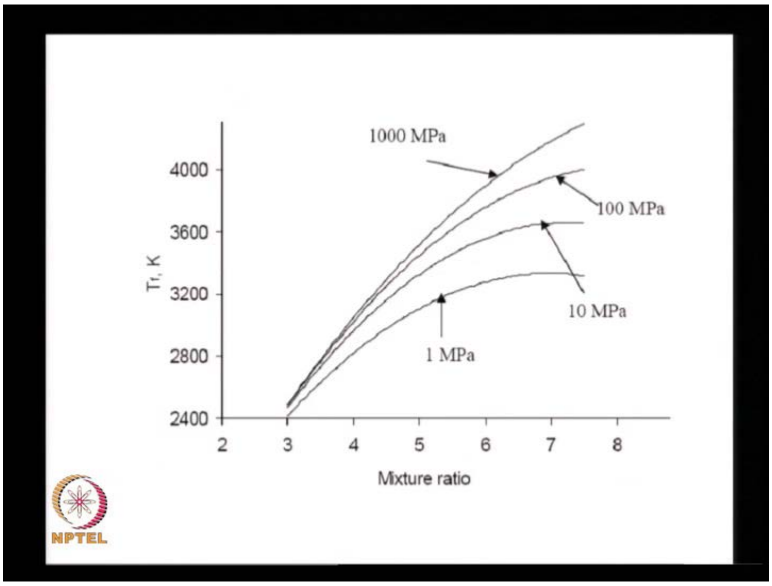

And let us take a look at the results again I did present this earlier. Now, let us see having understood the problem or having gone through it let us say how the flame temperature changes with mixture ratio for a hydrogen oxygen reaction. Mixture ratio 8 is storchiometric and as I said we always operate in the fuel rich region. Now, at higher pressure I find a higher value of temperature than at lower pressure. Why is it? At higher pressure you know the gases cannot dissociate because you are you are forcing the gases into a smaller region.

And therefore, you get more completed products of combustion at higher pressure and therefore, the temperature is higher as pressure reduces, I come to something like 10 bar that is 1 MP a the temperatures are much lower than at thousand MP a. Therefore, I find higher pressure the dissociation is less and I can get a higher value of flame temperature. See we are able to interpret now I mean understood the problem.

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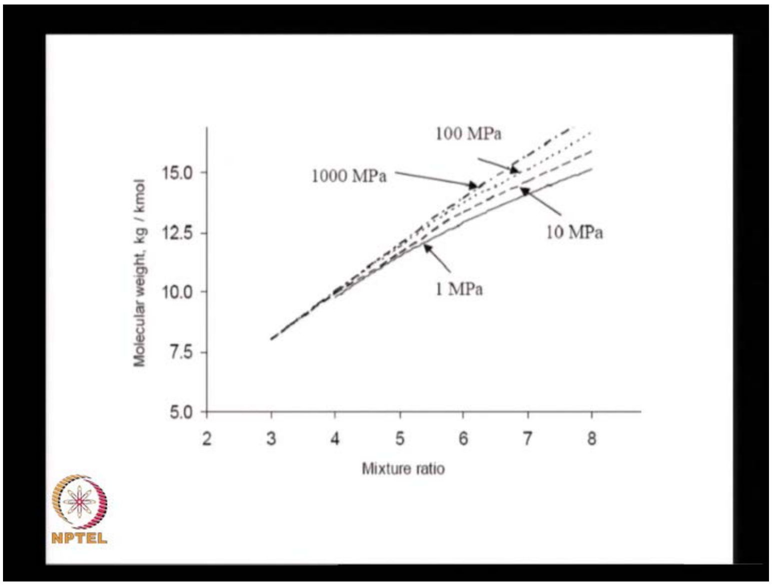

Let us came take a look at the molecular mass of the products? You find over here the molecular mass of the products increases, as the pressure again increases at 1 MP a it is evolving a little bit lower at a higher value of pressure may be I get a higher molecular mass why is it? Because I get more completed products of combustion, which cannot dissociate because of higher pressure it is I cannot have too many moles it is shrinking and therefore, my molecular weight also increases as the pressure increases. But I do find if I go back to my previous one, I find that the change in temperature is quite enormous whereas the change in molecular mass is little bit.

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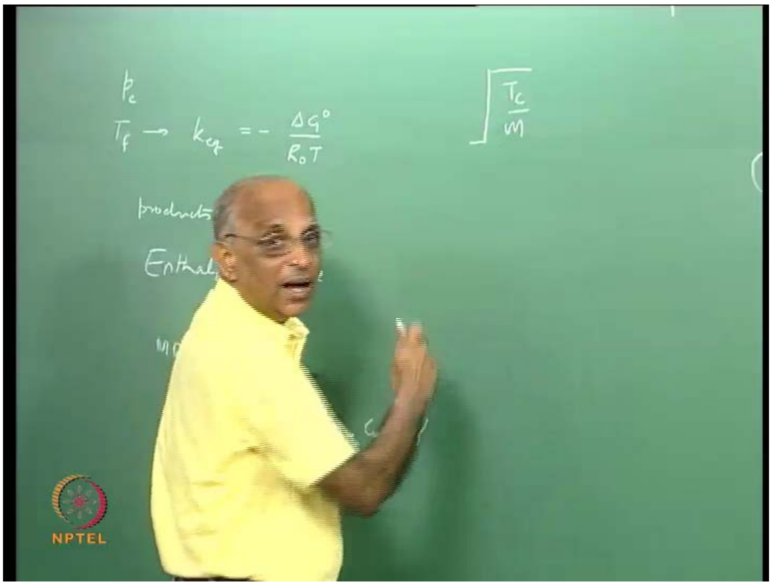

Therefore, the ratio of let us say under root T C by the molecular mass will still be large will still be higher at higher pressure and therefore, a higher pressure gives me a higher value of performance. Let us take a look at some more things, let us take a look at gamma we said for the simple specious like a mono atomics specious it was 1.67. For more complex things like C c l 4 and all that it was lower at 1.12 or something and what is it we find? We find that at higher pressure we have more complex products and therefore, the gamma is smaller as pressure reduces the value of gamma decreases, which is again in the direction now, I put the value of gamma everything together.

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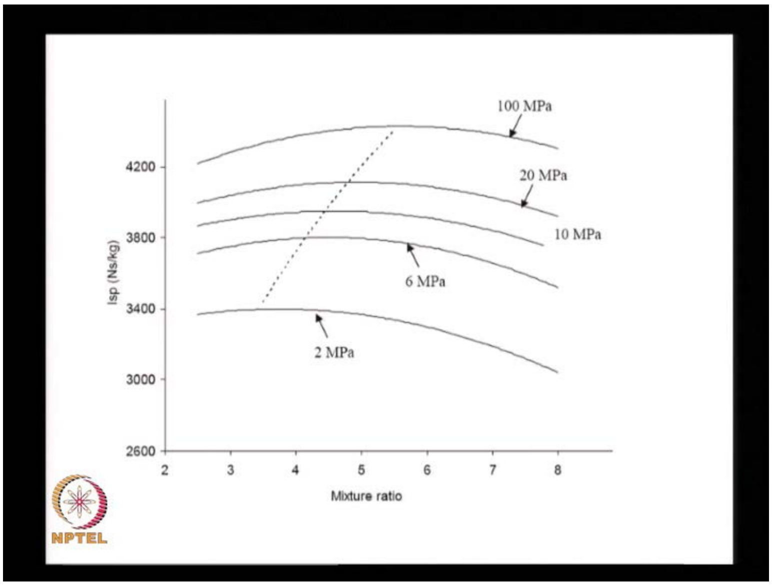

And calculate my I s p value I find well at higher values of pressure like what is shown hundred MP a. I get a higher value of specific impulse compared at a lower pressure. But something more important you know? The peak values is somewhere, over here at hundred MP a, at as the pressure decreases I get more and more fuel rich gives me a higher value that means, the choice of the mixture ratio. Which gives me maximum performance also depends on pressure because of the dissociation. I think these are the important conclusions which we draw from these particular slides. I think this is all I have about the slides and now, let us go back and try to understand the last part of why we do all these equilibrium analysis? As we say or there certain things which we need to understand further.

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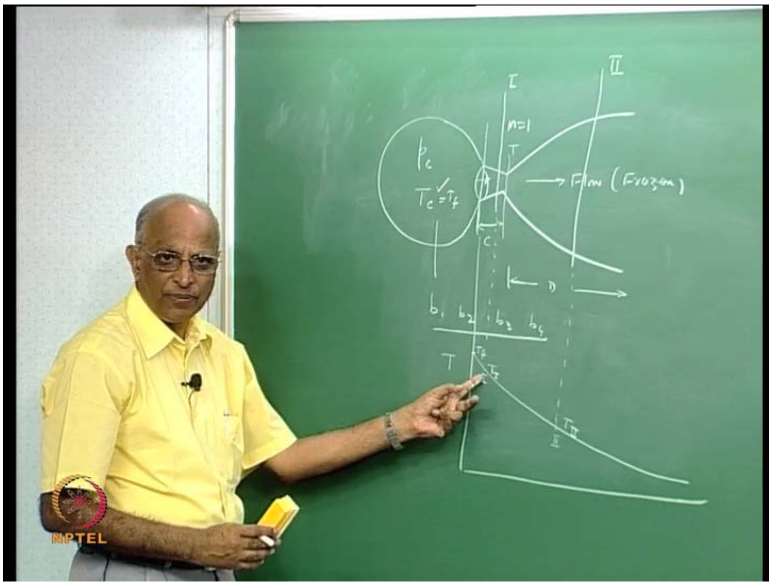

You know one thing I want to qualify is? When I put the I s p in that particular plot it is I s p at sea level, because we found I s p will change at sea level the ambient pressure is one atmosphere. Now, let us consider the last part of the dissociation before we can look at the chemical propellants for their characteristics. You know what is this we have been talking of? We have a combustion chamber wherein the pressure is p C the temperature is p C we know now, how to calculate T C which we said is adiabatic temperature. We also, know at this adiabatic temperature what is going to be the proportion of the product b 1 b 2 b 3 b 4 and so on?

All these products from the combustion chamber I deliberately use this, because let us not get let us not think that the rocket should always be a cylinder and all that. This is the combustion chamber this feeds into my nozzle the nozzle is like this, over here this is the converging part of the nozzle this is the throat the convergent and this part is the diverging part of the nozzle. I have what is it we have done so far? We have determined the products of combustion that is moles of the products the flame temperature as the gases enter the particular nozzle.

Now, what is going to happen what is going to happen to the flow over here? In our previous work on nozzles we assume yes I know b 1 b 2 b 3 b 4 here, I can calculate the value of gamma I can calculate the value of m, I can calculate the value of T C and using the relation I got I s p for one dimensional flow based on these products. In other words I assume that, the composition remains the same everywhere the value of gamma remains the same everywhere. The value of molecular mass remains the same everywhere, that means my flow is taking place flow through the nozzle is taking place as if the composition were frozen. And what did I determine and what did we determine? Let us plot it.

We determine the variation of let us say temperature from the adiabatic flame temperature which we have just calculated and as it goes on it goes this we have the throat at (( )) is equal to 1. But now, there is some certain difference. Now, as the flow takes place temperature drops therefore, let us take a section here now let me take a section over here, let us call it as section one let me take section two over here, just to illustrate the phenomena.

That means, I take this this is my section one of the nozzle that means, I take it in the convergent I again go ahead take a section in the divergent this is 2. At section one the temperature is let us say T 1, at section two the temperature is T 2 over here. Now, what is it I find? I find T here T 1 at section 1 the temperature is less than the flame temperature let us put it down, because this we need to be absolutely clear about it.

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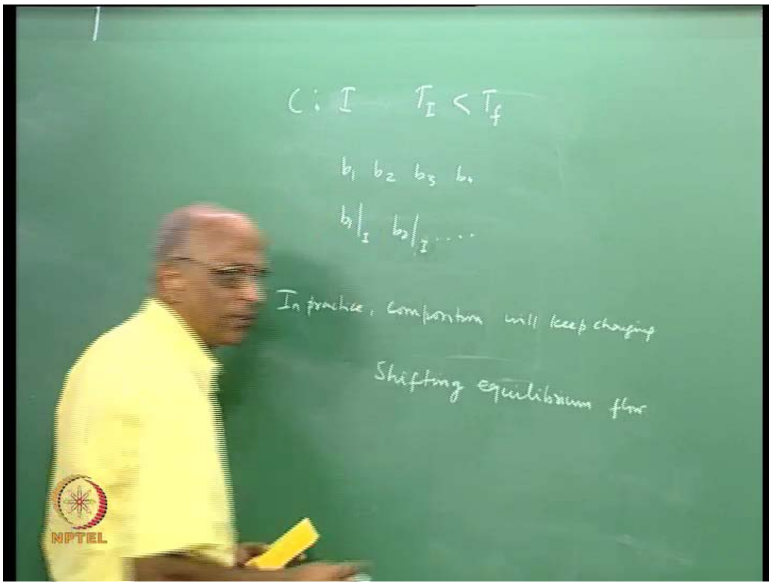

C : I $\quad T_I < T_f$

$b_1 \; b_2 \; b_3 \; b_4$

$b_1|_I \; b_2|_I \ldots$

In practice, composition will keep changing

Shifting equilibrium flow

That means, in the convergent when I had a section 1 the temperature was T 1 which is less than the flame temperature T f. If the products are going to be equilibrium at this section one well the proportion will not be b 1, b 2, b 3 and b 4 as we calculated at T f, but since it is cooler perhaps the composition will be different it will be b 1 corresponding to the new value of T 1 similarly, b 2 corresponding to the new temperature T 2 and T 1 and so on. In other words in practice at as the temperature gets lower, I will get a new composition here and when it has expanded quite a bit may be the composition will be totally different.

In other words the composition of the products b 1 b 2 b 3 b 4 and whatever, the heat for a given reaction they will keep on changing as the flow takes place. Therefore, I say in practice composition of the gases or the molar composition which we are considering will keep changing. As the gas expands I am going to get a new equilibrium constant and that is going to be a new type of b over there and how to I solve this? In other words the composition keeps shifting and such type of flow in which at each point the composition shifts is known as shifting flow shifting equilibrium flow. Because the equilibrium shifts I call it as shifting equilibrium and this is equilibrium flow.

Well to solve this is extremely simple? I go to the next section I find out what will be the temperature for this particular expansion assuming the values of gamma corresponding to the earlier section. I can find out at this point I find out the value of the new specious I can calculate what is my I revise temperature again revise products again and so on. I can do this in a chemical or let us say a shifting equilibrium. And what happens in shifting equilibrium? Because the temperature drops I get more of the products which are not dissociated, because at low temperatures I cannot get dissociated heat gets released.

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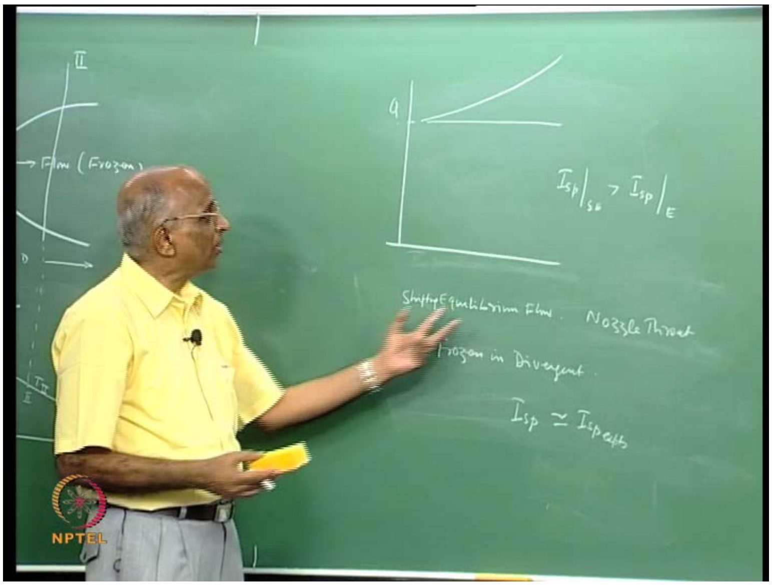

And therefore, if I were to plot my value of heat release which I release I took few of the combustion along the nozzle I do not consider heat release at all in practice, because of this heat gets released and (( )) gets released. And therefore, whenever I calculated the temperature distribution in the nozzle like this based on expansion actual temperature will increase. And therefore, because the temperature has increased my I s p, my value of specific impulse corresponding to shifting equilibrium will be greater than I s p corresponding to equilibrium. Is this point clear? This is important, but now how do I determine which is how should I use?

In my convergent the flow is quite subsonic and therefore, I have lot of time for reactions to occur in my divergent that the flow is supersonic there may not be time for equilibrium to take place. And the general practice what we find is well you assume equilibrium flow or shifting equilibrium flow, up to the nozzle throat and frozen thereafter and this seems to give, the value of specific impulse to be near the values what are experimentally measured. But this is not always true it depends on the type of gas the type of dissociation, but for hydrogen oxygen there has been published work they have bray model and all that, which assumes that just put it down.

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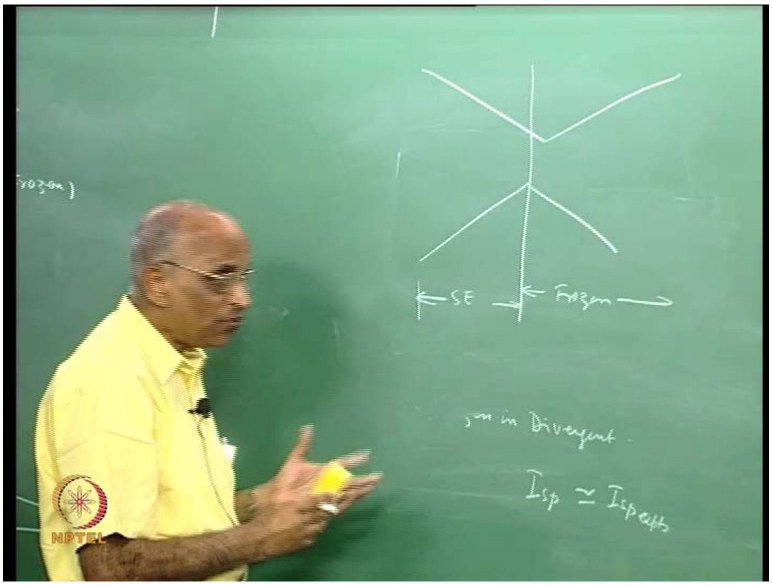

I Supposing I have a nozzle convergent followed by divergent I have in the convergent shifting equilibrium flow and in the divergent frozen, which tends to give me a reasonable value. If not what is going to happen to me? I have specific impulse which I consider let us just make a last plot of it.

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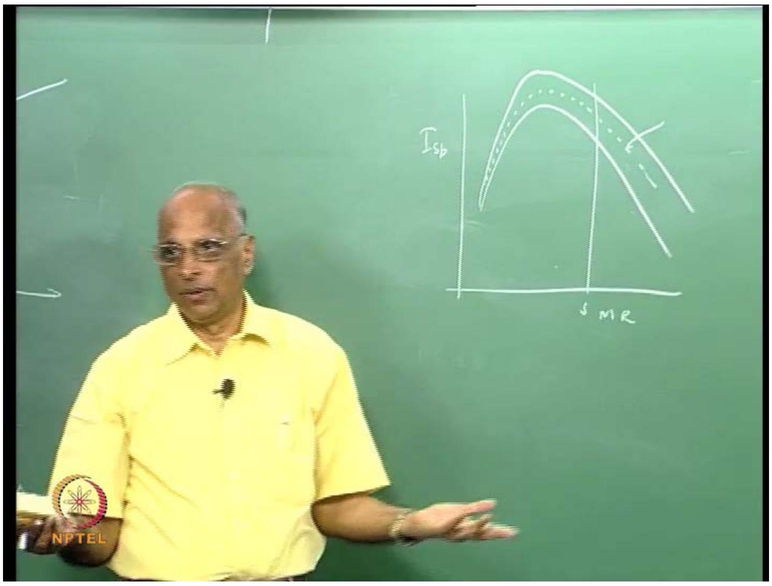

And then we will say what is mixture ratio? If I were to plot specific impulse this is my storchiometric this is fuel rich region in the fuel rich region I will get the maximum. This is for frozen flow for equilibrium flow may be I will get a higher value and they the actual will be in between the two. And this somewhat matches with equilibrium flow in the convergent followed by frozen in the divergent. I think this is all about dissociation of gases the characteristics of propellants we have seen and may be in the next class, we will take a look at the different types of propellants. Thank you.