Rocket Propulsion

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Module No. # 01

Lecture No. # 18

Dissociation of Products of Combustion

Good morning. We continue with the subject on dissociation of gases. Let me put the problem in a slightly different context. What do you mean by dissociation of gases? Supposing, you have H2O steam being formed in the product of combustion at high temperature, this will probably, may be the temperature is quite high, change into something like H plus OH. Because, this fellow cannot be stable at that high temperature. Therefore, if I burn hydrogen and oxygen and expect the combustion temperature to be large, may be, I will really not get H2O as a gas or stream but, rather I may get H plus OH and some mole of H2O. Now, the question is, how do I estimate this? When we did the simple calculation, we looked the Stoichiometry. When we looked the Stoichiometry, we said, the completely oxidized products of combustion, H2 plus half O2 is being formed. Like, we add C plus O2 which is equal to CO2, which is again completely oxidized products of combustion.

But, if the temperature or the heat released in this reaction is very high, then perhaps, I may still end up with H, I may end up with O, and I may end up with OH and may be other dissociated species. Similarly, carbon and oxygen, mind you, it, the composition could be different, could still be, we say Stoichiometry composition, but, at high temperature, it causes these species to be more dissociated. Instead of having final or a completely oxidized species, we get species which are dissociated species.

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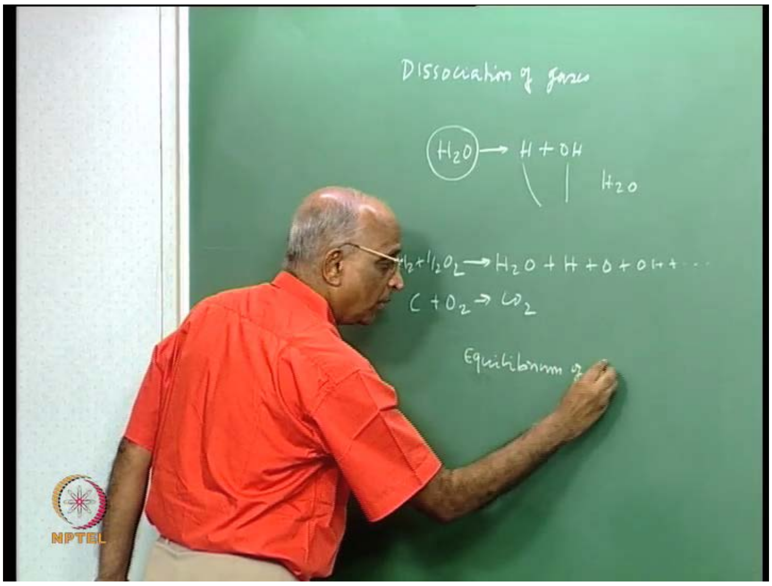

Therefore, how do you find the proportion of these things, is the question which we like to ask and we were talking about this. We said, well, we will do something like equilibrium of the products, which are formed. May be the products, may be the reactants together and see under what condition we can get this. This is what we are trying to do. For this, we introduce the word, Gibb’s free function and Gibb’s free energy and what did we find out. We found the d G, that is the change in Gibb’s free energy was equal to v d p minus s d T. We also asked ourselves some question. Supposing, I have a system in which, which not only does P d V work, but, I do some work on the system and this work was d zeta. Then, I got the equation as the change in Gibb’s free energy is equal to v d p minus s d t plus the incremental or the non P d V type of work. It is this non P V d type of work, what we are looking at. We want to make sure that, there is no net changes taking place. That means, no net further changes are taking place. I want to find out under equilibrium conditions, what is the type of species what I get and that is, what I want to solve. Namely, we are, therefore we said, if d zeta, that is the non P V d work is 0 and we are looking at d G at, let us say constant pressure, a constant temperature and then, what happens to me. This knocks out. So, d P is 0 under constant pressure, d T is 0 at constant temperature and I am left with the non, that is the non P d V type of work.

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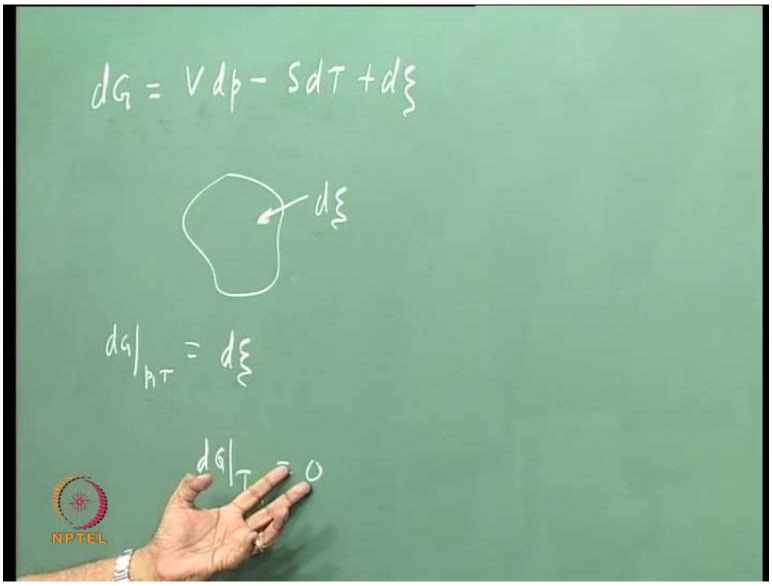

Since, no work is getting done on this system, well for equilibrium, we say Gibb's free energy at constant temperature and pressure is equal to 0. I think this must be clear to each one of us. The Gibb's free energy tells us, when the system is in equilibrium and what do we mean by equilibrium? No further changes are going to take place and we say the change in Gibb's free energy is 0 when, there is no no further changes are possible. And, when no further changes are possible, the composition of all these things remain invariant as it is. I think it would become clear.

Let me take one more example. Let me take the example because, this, the concept is little more involved. Let us say, I have a tank containing hydrogen. Let us say hydrogen gas. Let us say, it is at the room temperature of 25 degree centigrade, which is equal to 298 Kelvin. Now, I heat this gas to something like, let us say 2000 degrees. At 25 degree centigrade, only hydrogen gas is there. Let us say, pressure of this gas is equal to 1 atmosphere. I heat this gas to a very high temperature. May be, allow, may be the top here to be a freely floating mass less distance, instead of a container such that, the pressure is always 1 atmosphere here. I heat the gases to something like, let us say 2000 degree centigrade.

Mind you, the pressure I maintained constant because, this is the mass less piston. The ambient pressure is 1 atmosphere. The pressure here is still 1 atmosphere. Now, at 2000 degree centigrade, perhaps some of the hydrogen may change into H plus H. May be, part of the hydrogen may change. Supposing, I heat it to something still higher, let us say, I heat it to 4000 degree centigrade. Then, maybe, I may get more of this because, I know, I can dissociate hydrogen and I get more hydrogen. Therefore, now I ask myself a question, at 1 atmosphere and 298 Kelvin, the equilibrium is all hydrogen.

At 2000 degree centigrade, may be, I get a little bit of H and H atoms and more of it and some part of hydrogen or rather, if I were to look at the partial pressure of the gas, may be PH2 at 25 degree centigrade is 1 atmosphere and the partial pressure of hydrogen atom is equal to 0 because, everything is hydrogen molecule. May be, at 4000 degree centigrade, we will work out this problem today. What is going to happen? May be, the PH2 plus PH is still 1 atmosphere and therefore, it could be something like 0.4 atmospheres and this could be 0.6 atmospheres. Therefore, what is it happening? I am getting more and more of the dissociated species at high temperature.

Mind you, in a rocket chamber, the temperatures are quiet high. Instead of getting species like CO2 H2O and all that, I may start getting species which are broken into fragments, like OH, h and stuff like that. Therefore, I may not be able to get the entire energy to be liberated here. But, there is something else, which is extremely important that concerns the flow in the nozzle, which I will come back a little later. Is this clear and why we are doing this problem. If this is clear, let us go back to this definition. We said d G is equal to 0 at constant temperature and pressure for a single medium, for a single species. Now, I tell myself, this particular one d G, I wrote as d G is equal to v d p minus s d t and I am considering this. May be, let me forget about the equilibrium part. May be, some non P d V type of work being done here.

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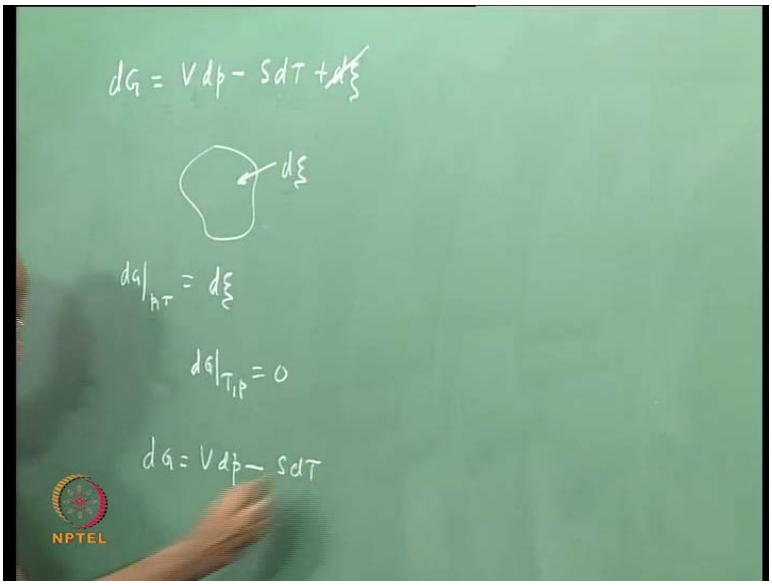

$$dG = V\,dp - S\,dT + \cancel{d\xi}$$

$$dG|_{nT} = d\xi$$

$$dG|_{T,P} = 0$$

$$dG = V\,dp - S\,dT$$

I asked myself, supposing I have d G coming from a variation in pressure V d P, minus a variation in temperature s d T and now, instead of having, let us say, here I saw a single component gas, a single component, I put a constituent. Let us say, a gas A and gas B. There are two gases. I want to know to define d G. What is going to happen? What is the number of moles of A? What is the number of moles of B? I tell myself, P a, plus partial pressure of species A, plus partial pressure of species B is equal to total pressure in this particular system. This is P. Now, as I heat the gases, I expect some increase in A and B depending on the equilibrium.

I have still not defined equilibrium, mind you and therefore, now I say, when I have a two component gas, the moment I put more of A, what I am going to do. I am going to change the value of d G by the number of moles of A I am putting. But, number of moles I am putting is, keeping B constant, I put d n a moles and therefore, the change in Gibb's free energy, when I add d n a moles of A, so by keeping B constant, I can write it this way. Similarly, I put some moles of B in this. I can write is equal to d G plus d n b, keeping A constant into d n b over here. For a multiple component system, like I have A and B, therefore, I say, in addition to changes in pressure and temperature, which causes the change in the Gibbs's free energy, now I also write, plus d G by d n a, keeping, now I keep these two also constant, pressure and temperature has to be kept constant, plus all the component B has a constant into d n a, plus I have d G by d n b keeping pressure and temperature constant and keeping now A constant into d n b.

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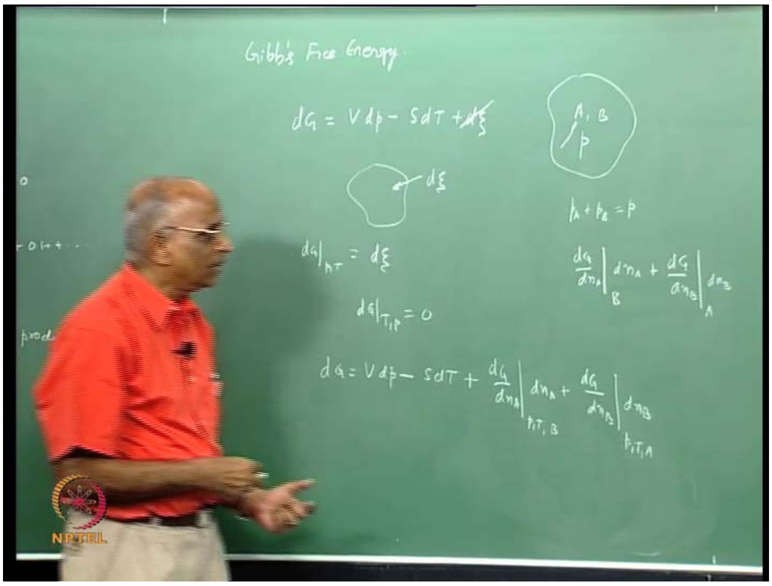

This particular term comes because, I have a multiple species system. Whereas, this part of the equation which we derived in the last class, was for a single component system. Now, I keep on adding, supposing I say, I have n components of the gas. Then, the equation slightly becomes a little more clumsy but, mind you, it is still the same. You say, d G is equal to, we have v d p minus s d t plus; what is it we are talking of. Let us put it in a general form.

We have d G by d n, let us say j into d n I. Let us say, what is it we are going to maintain constant? We are going, P to be constant, T to be constant and we are going to make sure that, j is not equal to I. That means, j is not equal to I. All other things are held constant, except the j constant. When, I say d n 1, this must be d n 1, when it is 2, it must be 2. Only that is changed and therefore, I can write it in this form. Now, I add all of them together and I make sure that I, goes from 1 to n.

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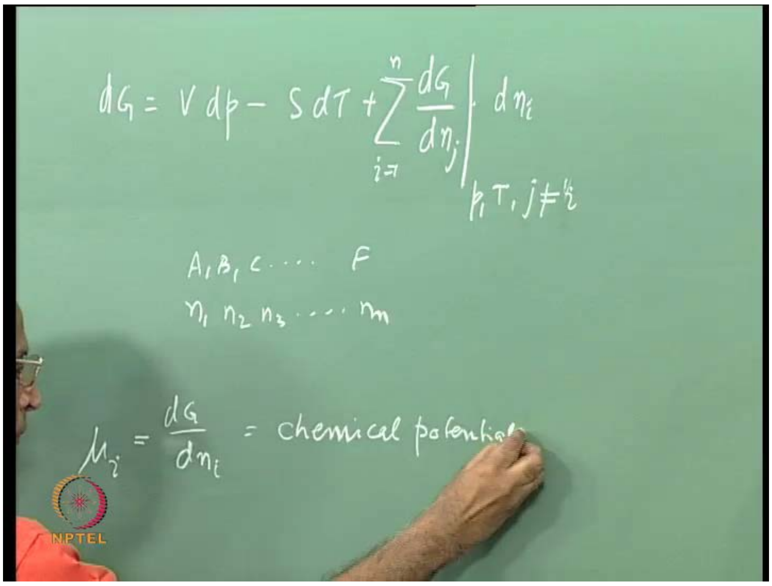

$$dG = V\,dp - S\,dT + \sum_{i=1}^{n} \frac{dG}{dn_j}\Big|_{p,T,j\neq i} dn_i$$

A, B, C .... F

$n_1\ n_2\ n_3 \cdots n_m$

$\mu_i = \frac{dG}{dn_i}$ = chemical potential

In a multiple component system, there we have species, may be A, B, C and all that to, may be, f or something. We have, this is n 1, n 2 moles, n 3 moles and so on, up to n m moles. I have just increased the two things to multiple things. Let us keep it a little gentle and what is this value of d G by d n j known as? You add per mole of I added, the change in Gibb's free energy is spoken of as chemical potential I. What chemical potential tells is, when I add 1 mole of, keeping all the mole same, no change in pressure, no change in temperature and that is what we call as chemical potential mu. If this part is clear, I can go forward and we can readily find out how to calculate the species that we are talking of. Now, I can now write my equation, d G is equal to v d p minus s d t plus summation of mu I into d n I.

Now, I want to simplify it further. At constant temperature and pressure, d G at constant pressure and constant temperature, I write this as equal to summation, let us say I is equal to 1. How many species are there? I write it as, maybe, I is equal to 1 to n of mu I into d n i or rather I can write Gibb's free energy at pressure and temperature is equal to mu I into n I. Summation is over all I's. Chemical potential into the number of moles is given me this at constant pressure and temperature.

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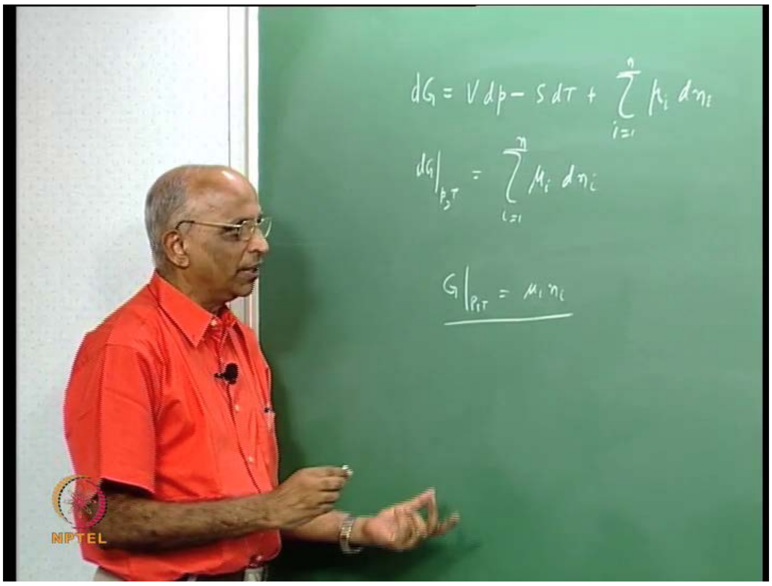

We will make use of this. We will define it and we will make use of this to be able to formulate what are the number of moles which of hydrogen and hydrogen molecule and hydrogen dissociated hydrogen atom, which are formed over here and extended to any possibility. Let us do that. For that, I will go back once again to the basic equation what we had here for a single species. I have to relate it to partial pressure and that is where my problem is. That is what I am trying to do. We have d G is equal to V d P minus s d T.

Supposing, I were to say, d G by, let us say I found d T and why did I do this? I am interested in finding out the composition of a gas at a particular temperature. Therefore, at a particular temperature, I am looking at the value of d G by d P at constant temperature. If I do this, well, the temperature is constant. This gets knocked out and therefore, I get d G by d P is equal to V. Is it all right? You know, I think we will be clear.

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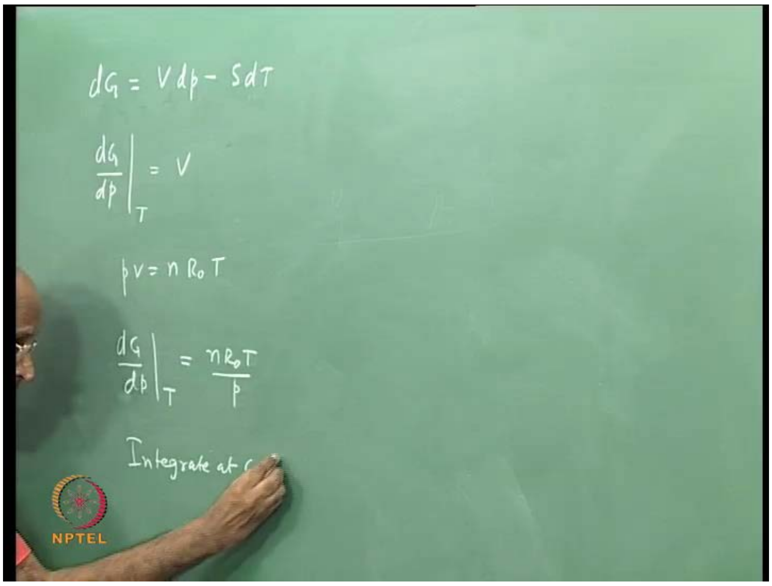

But, from ideal gas equation, we know P V is equal to the number moles into universal gas constant into T. Let us be very clear. P V is equal to m r T specific gas constant; n into universal gas constant r naught into T. Therefore, I can write this particular equation as equal to d G by d P at temperature is equal to, I now say, V is equal to n r 0 into by P, d G is V n r 0 T by P. Now, if I were to integrate this equation at constant temperature, that means, I again integrate at constant temperature for a pressure change from a value, say reference value P reference to a partial pressure P. We get the Gibb's free energy G as equal to n r 0 T ln P, going from P reference to the pressure P.

The standard reference of P value of P reference is taken as 1 atmosphere generally. Assuming this value, assuming the value of G corresponding to the the reference pressure as G naught, we can now write the value at any partial pressure P as equal to G is equal to the value of G naught over here or rather I get, G is equal to G naught plus n r 0 T ln P. We must remember that this G naught, I should have put the reference value, that is the 0 as as a suffix rather than as a suffix. This is how it is done. The standard value at G naught is given in text books at the temperature T and at P at at the reference value of pressure.

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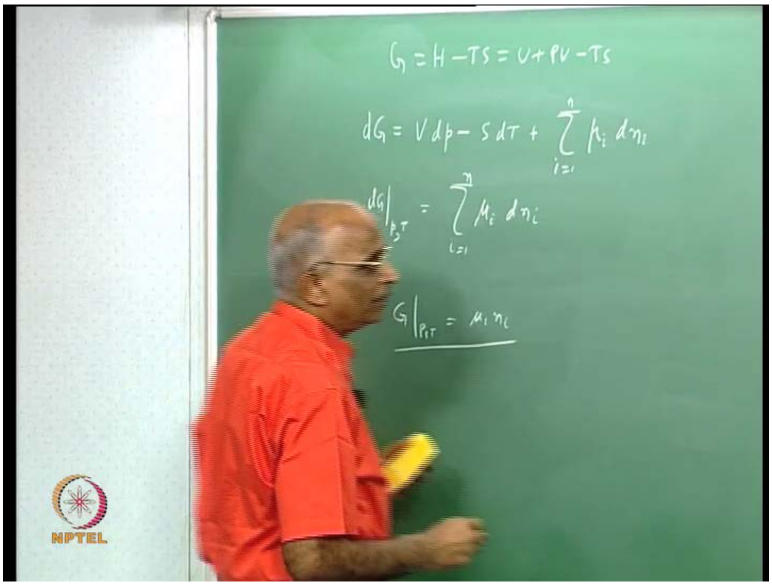

$$G = H - TS = U + PV - TS$$

$$dG = V\,dp - S\,dT + \sum_{i=1}^{n} \mu_i\,dn_i$$

$$dG\big|_{P,T} = \sum_{i=1}^{n} \mu_i\,dn_i$$

$$G\big|_{P,T} = \mu_i n_i$$

Having said that, now I look at this form of the equation and what should be the unit of G. G has units of H minus T S or U plus P V minus T S. That means, it is units of energy. Therefore, G has units of kilo joule. May be, I learnt to do it in terms of G by n is equal to G 0 by n plus r 0 T ln of P. Therefore, I call this now as my G. This, I call as G naught plus r naught T ln P, where the unit of the Gibb's free energy which I am going to use henceforth, will be so much kilo joules per mole.

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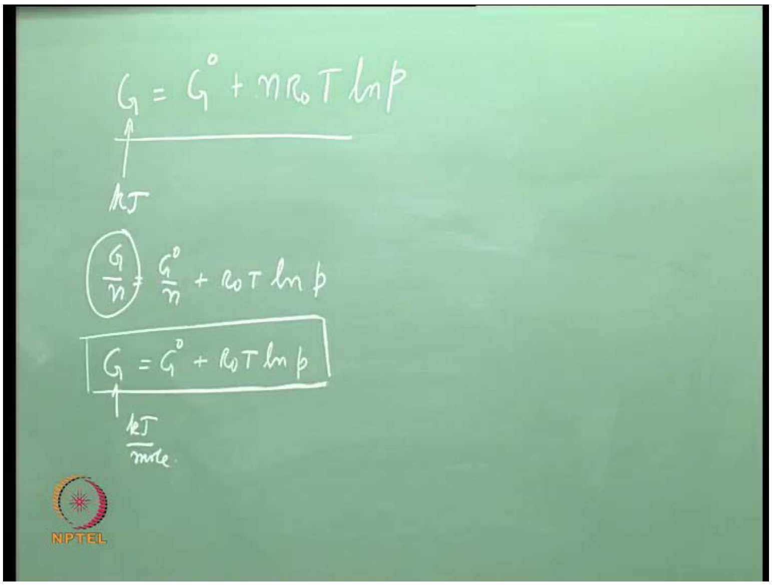

$$\underset{\uparrow\ kJ}{G} = G^0 + nR_0 T \ln P$$

$$\frac{G}{n} = \frac{G^0}{n} + R_0 T \ln p$$

$$\boxed{\underset{\uparrow\ \frac{kJ}{mole}}{G} = G^0 + R_0 T \ln p}$$

I would rather have a per mole rather than for the total, and this whole thing is for n mole. Per mole is what I get over here. Now, let me take a look at this equation and let me take a look at this particular equation which is, Gibb's free energy is equal to mu I. Therefore, here also I find G, so much kilo joule per mole at constant pressure and temperature is equal to mu I.

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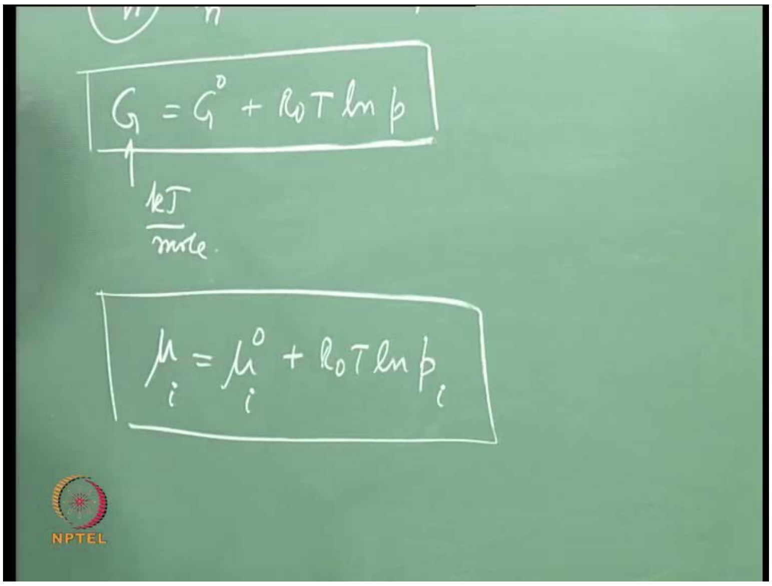

Therefore, I can also write based on this equality, I can write mu chemical potential is equal to mu 0 plus r naught T ln of P, ln of, I get higher constituent partial pressure over here. This is the equation for the chemical potential. Therefore, what is it? Let us put down whatever we have done so far. So is, that we can draw these things little later. We have written that mu I is equal to mu I at standard plus r naught T into ln of P i. Just in the same way, G is equal to G naught plus r naught T into ln P. Well, this is for a single constituent. Here, I have extended to a multiple wherein, I have i and for the higher constituent (( )).

We want us to get a little more physical understanding. Let us go back to this problem of, let us say, I have a gas. Let us say, may be a constituent. Let us say hydrogen, a constituent H over here. I heat the hydrogen gas at constant pressure as it were. That means, I have a mass less pistons surrounding here and ambient pressure is 1 atmosphere. Since, its mass less and friction less and the pressure here is 1 atmosphere, I heated and I tell myself, when I heat a gas, I write this equation H 2 becoming H plus H at a high temperature. But, at high temperature, H plus H is also going to combine to give me hydrogen. Therefore, I should be able to really write this equation as H 2. In the forward direction it goes like this and in reverse direction it comes as H plus H. What is my aim? To find out how much of H and how much of H 2 is there in this particular gas.

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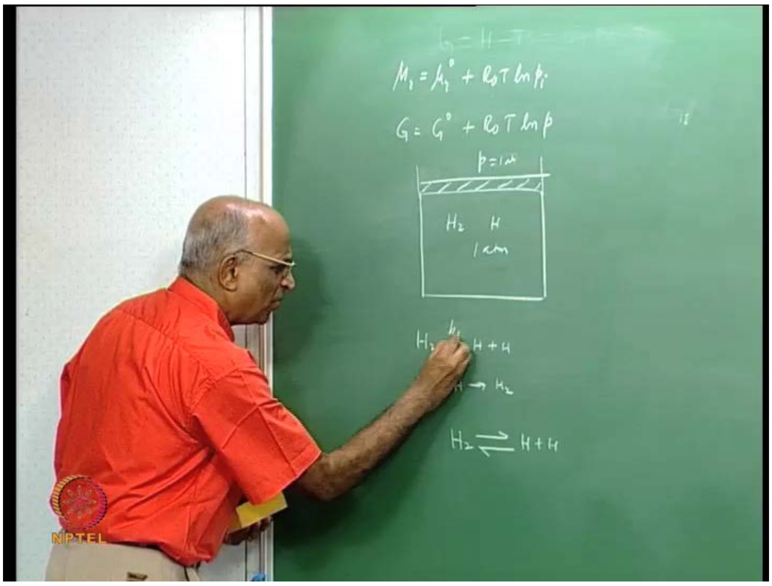

This is what I want to do. How do I do this? Now, I say, let the reaction rate constant for this forward reaction, that is the kinetic rate constant for hydrogen being converted to H and H, I call as small k f.

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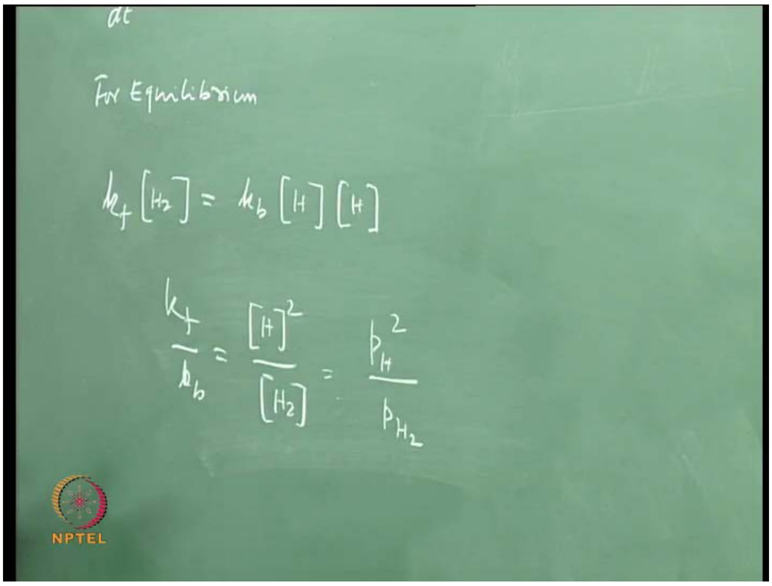

All of us, when we studied combustion, we say, we use the law of mass action. What is the law of mass action do? The law of mass action says, that the rate of the reaction, let us say, the rate at which the active concentration of H 2 changes with time goes as a constant into the value of the species itself. That is the rate of a reaction is proportional to the active concentration over here. That means. I say d H 2 by d T, it keeps depleting.

I have minus k f into H 2 over here. I want to write the same reaction for this reverse one. I say, yes, forward reaction is k f backward reaction is k b. I can write, the rate at which d H changes with respect to d T goes as k b into, I have two of this, H into H over here. Mind you, according to this reaction, this also keeps decreasing. Therefore, now I tell myself, that means the reaction proceeds in this particular direction. The reaction of H plus H proceeds in this direction.

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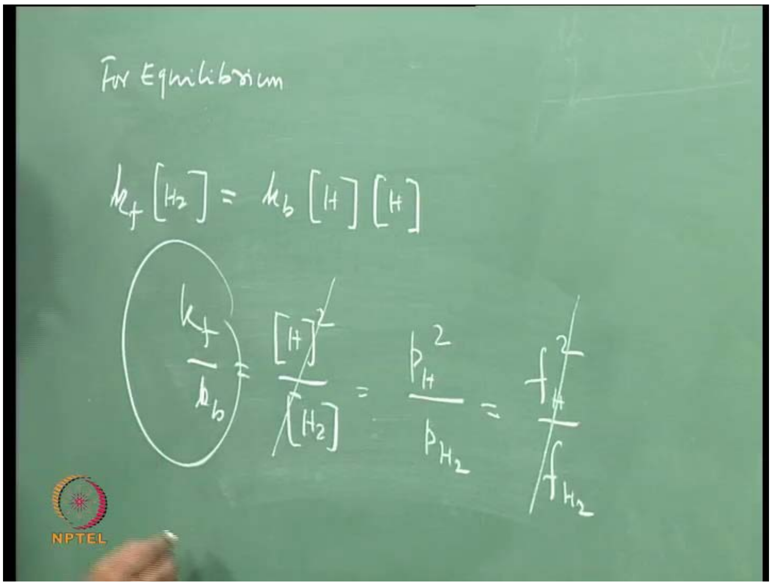

For Equilibrium

$$k_f [H_2] = k_b [H] [H]$$

$$\frac{k_f}{k_b} = \cancel{\frac{[H]^2}{[H_2]}} = \frac{p_H^2}{p_{H_2}} = \cancel{\frac{f_H^2}{f_{H_2}}}$$

Therefore, the rate at which hydrogen gets depleted is propositional to the hydrogen and the rate at which the H atoms get depleted, because of the reverse reaction is in this. Therefore, for equilibrium, the rate of these things must be the same. Therefore, I can write k f of H 2 is equal to k b of H into H or rather, I can write now k forward divided by the backward reaction is equal to H square divided by H 2. What is H and H 2? The concentration or we say the law of (( )) says, it must be the active concentration. But, in many reactions, we normally take it to be the total concentration of the substance.

For a particular reaction, instead of writing concentration, I can also write it in terms of partial pressure hydrogen square divided by the partial pressure of the hydrogen because, the concentration of hydrogen of H atom is going to be proportional to the concentration over here because, it is a given volume. In a given volume at a given temperature, we say how is partial pressure? Define? Let us put that down again. We tell ourselves from the ideal gas equation, P V is equal to n moles into r T, concentration is defined as n over V, which is equal to n over V is equal to P by r T and for a given pressure and temperature concentration to this pressure.

Therefore, we find concentration. For a real gas, you all would have studied about fugacity, which is the real pressure of a non ideal gas may be, fugacity of hydrogen square divided by fugacity of hydrogen. Well let us not forget into fugacitys' and concentration. Let us just look at partial pressure and we were interested in finding out, when we have hydrogen and hydrogen atom at 1 atmosphere pressure, what is the partial pressure of the hydrogen molecule and what is the partial pressure of the hydrogen atom. This is what we wanted to solve. Now, we tell ourselves, well the forward reaction divided by backward reaction goes as this and this particular term is what is termed as equilibrium constant, known as k equilibrium.

Therefore, having defined this, let us write out what is the expression. For the particular case of H 2 going to 2 H, I can say that the equilibrium constant of the reaction, which I say k suffix equilibrium is equal to P H square divided by PH 2. This is the definition of equilibrium constant. Any reaction, you say under equilibrium conditions, it goes as PH square by PH 2 or rather, if have I a set of gases, may be A, B, C, D, E which is reacting. Supposing, I have A molecules of a, I have b molecules of b, I have small C molecules of C, I have small d molecules of d, I have small e molecules of e and all that and these things come from a reactant.

Let us say, I have a reaction in which, let us say some reactant r r 1 with r 1 is reacting and with r 2, with this is reacting to give me all this. The equilibrium constant of this particular reaction, I can now write as equal to, I have P a 1, partial pressure of a 1 to the power a, partial pressure of b, b no I am sorry, partial pressure of a to the power a, a moles, partial pressure of b to the power b. Similarly, partial pressure to the power C and so on divided by partial pressure of reactant r 1 to power r 1, partial pressure of reactant r 2 to power r 2. In other words for simplicity, I can write it as product. That is product of, let us say, the products P I to the power ni divided by the product of the reaction. May be this is for the products. For the reactants, I have P I power n I. Some smaller way of writing, which is the equilibrium constant of a particular reaction.

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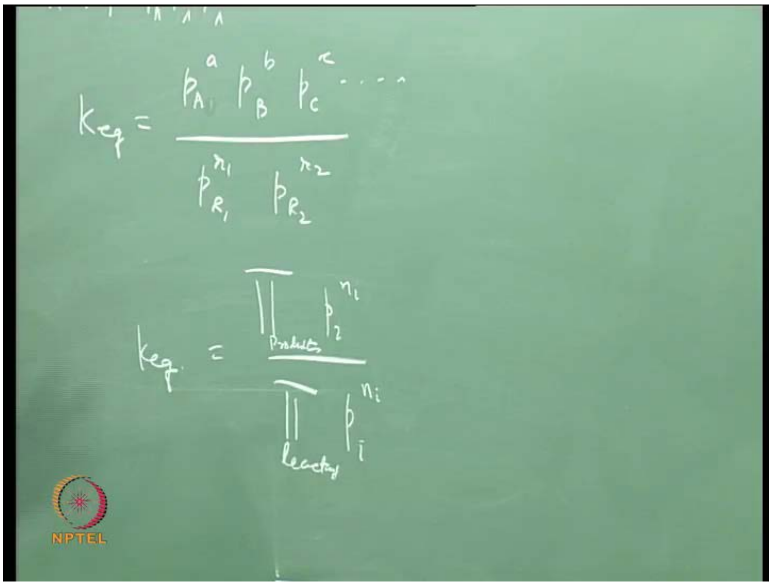

$$K_{eq} = \frac{p_A^{a}\, p_B^{b}\, p_C^{c} \cdots}{p_{R_1}^{n_1}\, p_{R_2}^{n_2}}$$

$$K_{eq.} = \frac{\prod_{\text{Products}} p_i^{n_i}}{\prod_{\text{Reactants}} p_i^{n_i}}$$

Now, I just want to spend another two minutes on what besides this. See, we have still not analyzed our problem. What are the problem we were considering as an example? We were considering the problem of, let us say hydrogen enclosed in a particular volume at constant pressure, that means, the freely floating piston. I want it to find out, what is the concentration of H and H 2 at a given temperature, may be at a given high temperature. Let us go back to this problem. But before that, may be, I need the, if I know the value, let us write it out. What did we get for this particular H and H 2? Let us write out. We had k equilibrium is equal to P H square divided by P H 2. What do we find from this? If the equilibrium constant is a large number, then dissociated species will be higher.

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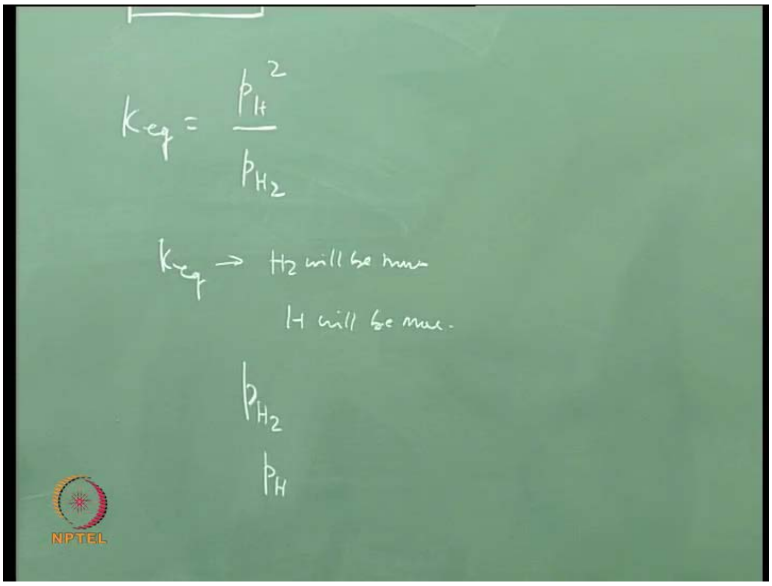

If the equilibrium constant, this is small number, very small number, then the denominator will be a large number. That means I tell myself, well, equilibrium constant gives me immediately a view of whether H 2 will be more or H will be more. But, how do I calculate it? I want to calculate the value of P H2 and the value of P H. This is what I want to do. But, I know, I, but, I can use k equilibrium and do that. Therefore, let us find out how I get the value of k equilibrium. Therefore, what is it we have defined so far? Let let us quickly revise what we have done such that, we we can build upon it.

We told ourselves k equilibrium is equal to, maybe, we are looking at, may be the partial pressure of products to the power of the moles divided by, may be for the products let us say, partial pressure of reactants to the power of the moles of the reactant. This is all what we are saying and this is the product and this is the product over here. Now, I want to get the value of k equilibrium. Let us take this simple example. Let us take the example of a species A going to a species B. See, I am very particular that we must have different ways of doing it.

I keep telling in terms of reactants, r 1, r 2 and may be products so that, we can immediately guess or be able to do any problem. Let us consider a reaction in which hydrogen H 2 as A, H as B over here. Now, what is happening? The value of k equilibrium, I want to find out for this reaction. But before that, I have a problem. I tell myself, look here; in this reaction d n a moles of A gets consumed. That means it is getting consumed.

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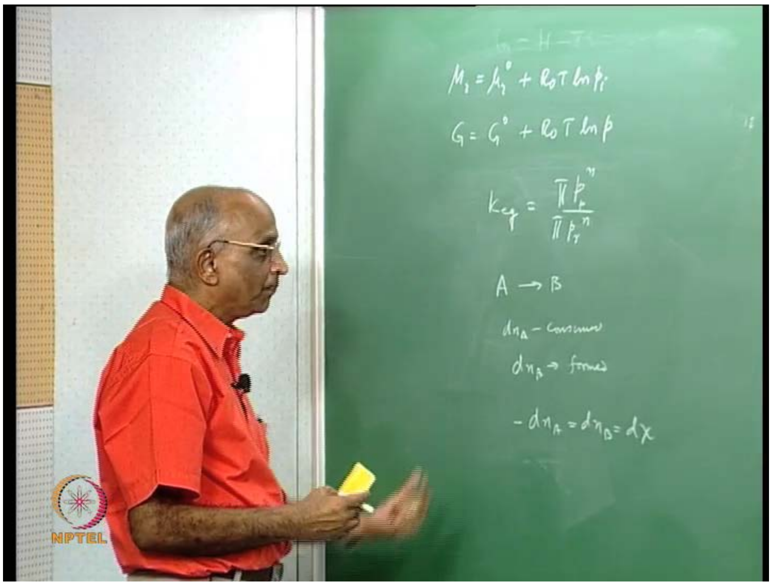

What is happening is, d n b moles of B is getting formed. But, since it is a 1:1, the number of moles here is 1. The number of moles here is 1. Therefore, I should also get d n a, which is minus, is equal to d n b which is, say is d Kye. The magnitude has to be the same because, this is 1. May be, if I remove something that may get manifested here, therefore, it is equal to d Kye here. Therefore, let us write the value for this particular reaction. Let us take back and put the value in terms of the chemical potential over here. Now, what is the value of the summation of mu over here? mu is equal to, the mu for the species A and B put together is going to be d n a is getting formed. Therefore, I can write it as mu i dot plus r naught T into ln of P a. This is the value of mu for this and what is going to happen? It is going to get converted or the the value of chemical potential of b is going to be, plus I get, I will come back to filling this gap. But then, I look at the change in the number of mu. May be, what had happened is, the changes which are taking place in the chemical potential corresponds to minus d n a or which I say, I can now write d n a as equal to d Kye and d n b as equal to plus d Kye because minus sign over here.

Therefore, I get something like I have the value of minus d kye here and the value as d kye here. That is the net change in chemical potential which is taking place or rather, this should have been the change in chemical potential or the change in the Gibb's free energy or let us just keep quiet. We will just say, well, the mu, I can write it in this particular form.

Therefore, but I tell myself that this is the value of the changing d mu. Let us keep it d mu which is same as the same in Gibb's free energy d G. I will again repeat, since I made some summary changes over here. I get mu is equal to mu i. The change in mu is equal to this into the number of moles of change. The change in Gibb's free energy for the product b is this into the d n b which is changed. The change in mu is essentially the change in Gibb's free energy because, we saw this and this were equivalent. Therefore, I can write that d G is equal to this. For equilibrium, I have d G is equal to 0 and what is the value? Even if we are not bothered about this one, we still have, may be mu a plus r naught T, r naught T into ln P a. We have this and therefore, I get mu a minus mu a plus mu b plus r naught T into ln of P b by P a is equal to 0.

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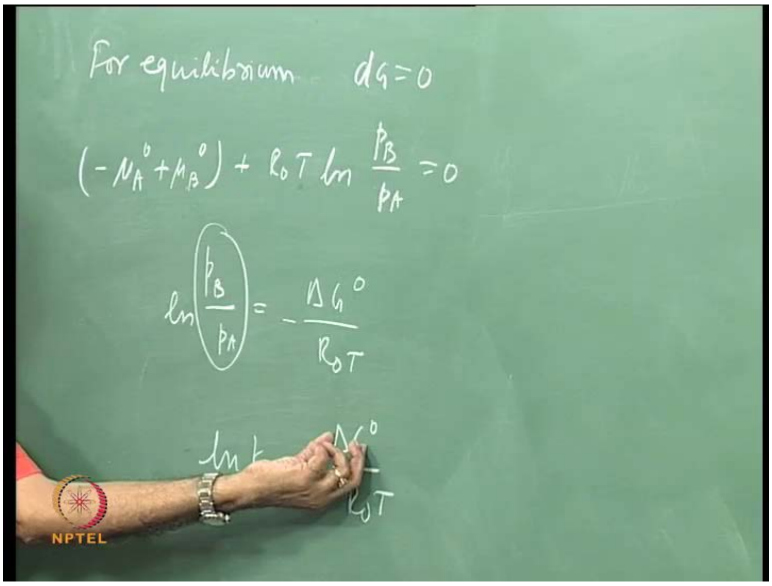

Or rather, now I get the value of the product divided by P a into ln of this is equal to, this becomes my change in the Gibb's free energy. Mind you, this is standard and this is standard. Therefore, it is equal to a standard here and now, I bring r naught over here. This is kilo joule per mole. This is again kilo joule per mole Kelvin into Kelvin kilo joule per mole. This P b by P a is a partial pressure of product divided by partial pressure of reactant and this is equal to ln of k equilibrium is equal to delta G 0 by r naught into T.

There must be something more to it. You know, I get the change here and I get this over here.

Therefore, mu b minus mu a, therefore, it must be something like minus delta G by r T, is what is the value of ln k equilibrium or let us keep in mind, I am relating the change in k equilibrium to the change in the standard Gibb's free energy over here.

Let let us try to understand it through a problem and then come back to this. Let us go back to this problem we wanted to do. If we take any book on combustion, the values of Gibb's standard Gibb's free energy at a given temperature is given. I will take the values of this from from one of the books we you all use very often. The book is by Turns, S R Turns and the name of the book is Introduction to Combustion. All all combustion (( )) give the value of delta G for the different substances and I think, this book, the second edition or the new edition came out in 2006 and we have a large number of copies in the different labs. Therefore, it is easily accessible.

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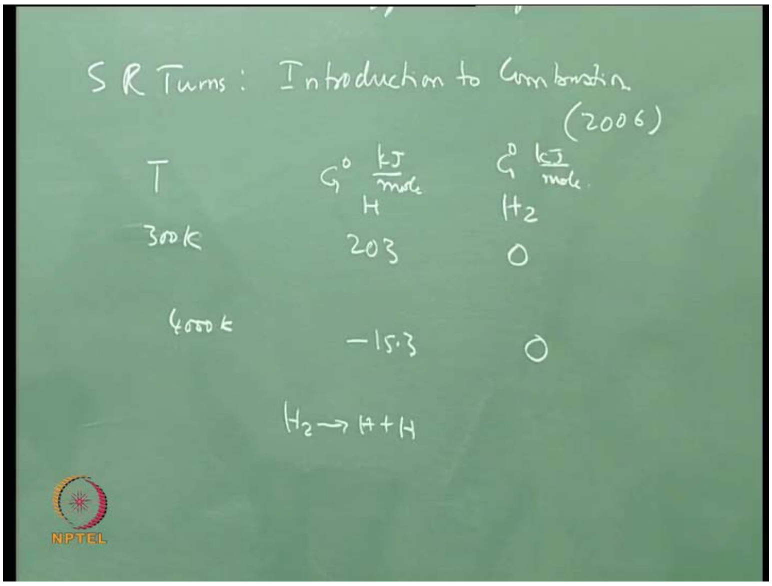

S R Turns : Introduction to Combustion (2006)

T	$G^0 \frac{kJ}{mole}$ H	$G^0 \frac{kJ}{mole}$ H_2
300 K	203	0
4000 K	−15.3	0

$H_2 \rightarrow H + H$

If we are going to look at temperature, I will just take two values. I take the value of at at let us say 300 Kelvin and I take the value at, and let us say 4000 Kelvin. The value of G naught, that is the standard Gibb's free energy at 300 is given in terms of kilo joule per mole is equal to 203 for for hydrogen atom. For H 2, it is 0 and at is again G 0 kilo joule per mole. At 4000, the value is minus 15.3 kilo joule per mole and it is again 0. Therefore, now if I wait to find out the equilibrium constant for the reaction, let us say H

2 going to H plus H, then I am going to take the value of delta G. That is delta G and let us lets lets put it together on this part of the board, ln k equilibrium at let us say 300 Kelvin is equal to minus delta G naught by r naught T.

This gives me the value as equal to 203 into joules 8.314 into something like 300. That is the change for the reaction H 2 to H, this is the value. Whereas, if I were to write the value of ln k equilibrium at 4000 Kelvin, if this the same thing going to give me the value minus over here and the value becomes plus, we say 15.3, that is 15300 divided by 8.314 into 4000. Therefore, now what is it we observe? We observe that the value at 300 ln k equilibrium is large negative quantity and k equilibrium is therefore, a very small number. Therefore, what we get is more of hydrogen will be available and the proportion of hydrogen, I can always calculate because, I know the value of k equilibrium from this equation that this is equal to P H square divided by P H 2. I can find out the proportion of PH 2 H 2 from this.

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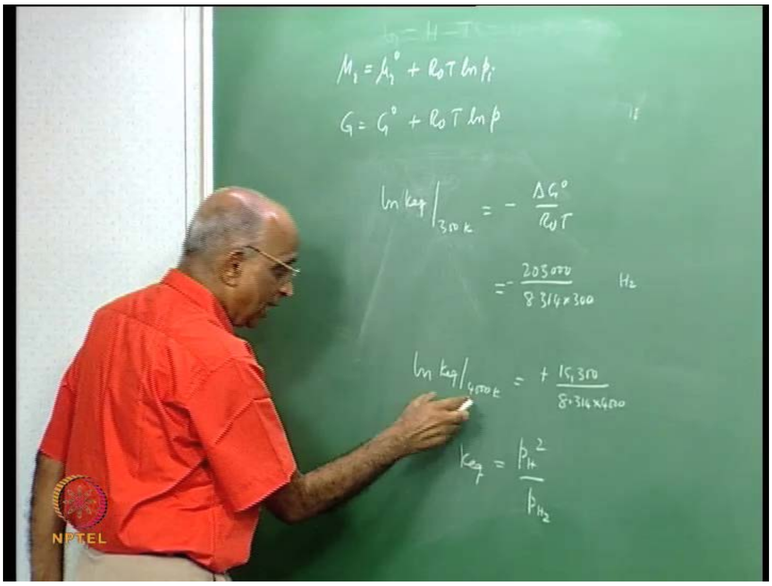

At the higher value of 4000, I get the value as 15300 divided by this, which is a positive number. In other words, a positive or large positive value of equilibrium constant tells me that the proposition of the products is much higher. Let us do one or two small examples and still get this notion little more clarified. See, actually ln k equilibrium will never be positive or negative. When I say ln k equilibrium is negative, all what we are saying is k equilibrium is a small number. When we say ln k equilibrium is a positive sign, then k equilibrium becomes a larger number. Even though that means, when I say a negative quantity, k equilibrium becomes a very small number and therefore, P H 2 is larger. When I say k equilibrium is a positive number, well, the value of the ln k equilibrium is a positive number, well, the products are larger.

But, why is it we are considering all this? It is not only, before I go back and show some results, we must remember that any any combustion chamber, the temperature of the products of combustion is quiet large. Therefore, I can get dissociated species over here. What do we mean by dissociated? I get CO; I get CO 2; I get may be something like O o O here; I get, may be carbon in the solid face over here, which is dissociated. I get H and I get O H and all that over here. Now, let us go to the next step.

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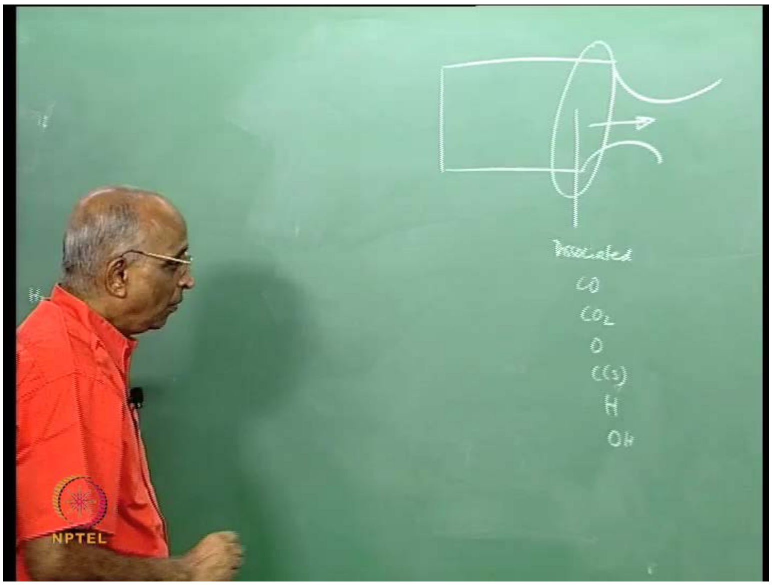

This dissociated gas, I know how to calculate. We will do it through an example. Now, I expand these dissociated gases in a nozzle. What happens? I expand the gases. Let us say again, I have the dissociated species expanding in a nozzle and what happens in a nozzle. As the expansion takes place, the temperature keeps falling because, it is expansion. Therefore, the density falls and the temperature falls and the speed or velocity increases. Now here, the temperature is very high. Therefore, I get all these dissociated species. As I move down stream of the nozzle, what is going to happen? The temperature falls. If the temperature falls, may be the dissociated species are going to combine to form the species again. That means, if I were to plot the heat release during nozzle flow, what is going to happen is, as temperature falls, the amount of dissociated species get decreased and for equilibrium to take place, what is going to happen.

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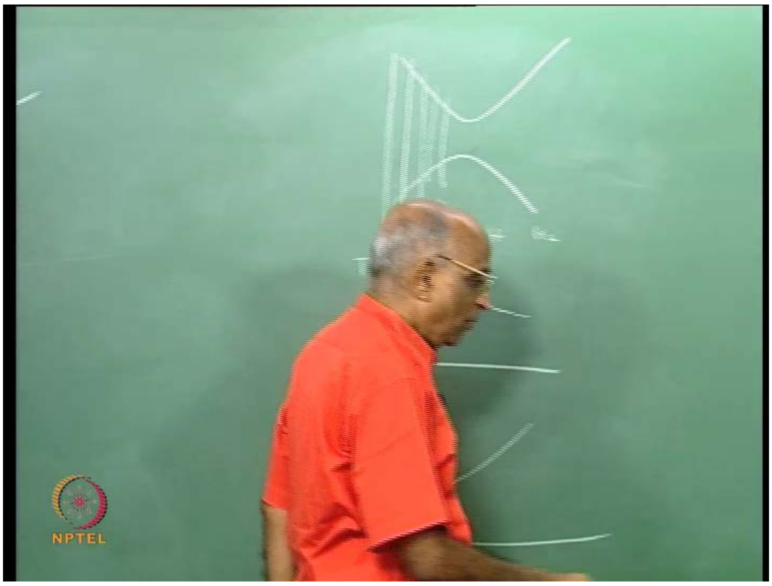

I am going to get more complicated things like, H may not be there. I will start getting H 2 again, which is more full and the heat gets released. Therefore, may be the heat release will take place in the nozzle itself. In other words, as the flow takes place in a nozzle, I get equilibrium which is shifting at each point. At this point, I get all dissociated. Here, I get the equilibrium, which is not that much dissociated here. I get equilibrium which is still not dissociated. In other words, what is it I get? I get a shift in equilibrium as the flow takes place in a nozzle. But, if a shift in equilibrium takes place, what is going to happen? I am going to get some heat energy. Therefore, such type of cases, wherein I have equilibrium taking place in a nozzle or a chemical equilibrium is known as shifting equilibrium. As compared, what did we consider earlier? We just took the properties or the entry to the nozzle and what were the properties.

We took TC and we took the molecular mass of the products. We took the gamma of the products and we worked out, what is the jet velocity. But in practice, with shifting equilibrium, what is it going to happen? I get more heat release and molecular mass is going to change. Therefore, my V j must be higher. Therefore, compared to frozen which we considered earlier, that means we considered frozen flow in the nozzle. Now, we are talking of shifting equilibrium flow in a nozzle. I will get more heat release and therefore, my I s p will go up. I think I have to consider this in further details with some figures to you. But therefore, a nozzle flow is not simple after all. If I have chemical reactions taking place, because the equilibrium is changing at each particular point and I get heat release taking place at each particular point.

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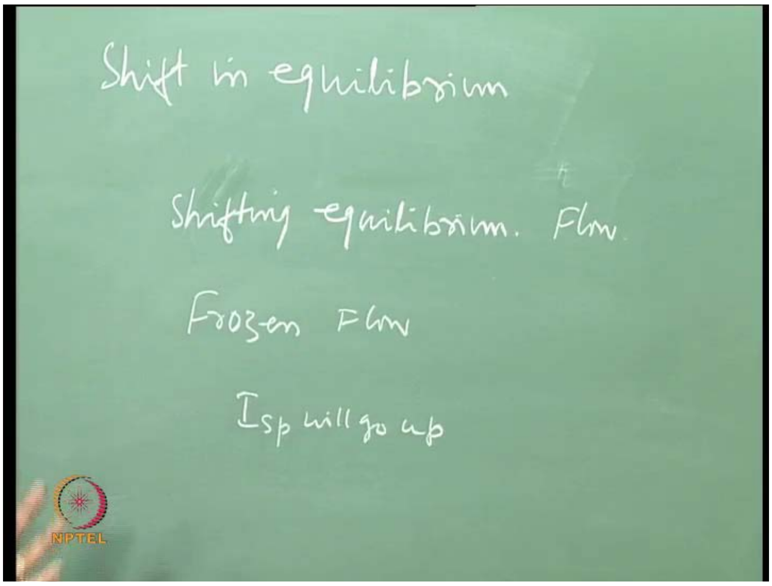

Shift in equilibrium

Shifting equilibrium. Flow

Frozen Flow

I_{sp} will go up

Therefore, recombination takes place giving me a net higher value of the specific impulse. We will keep this in mind. Let us do a problem.

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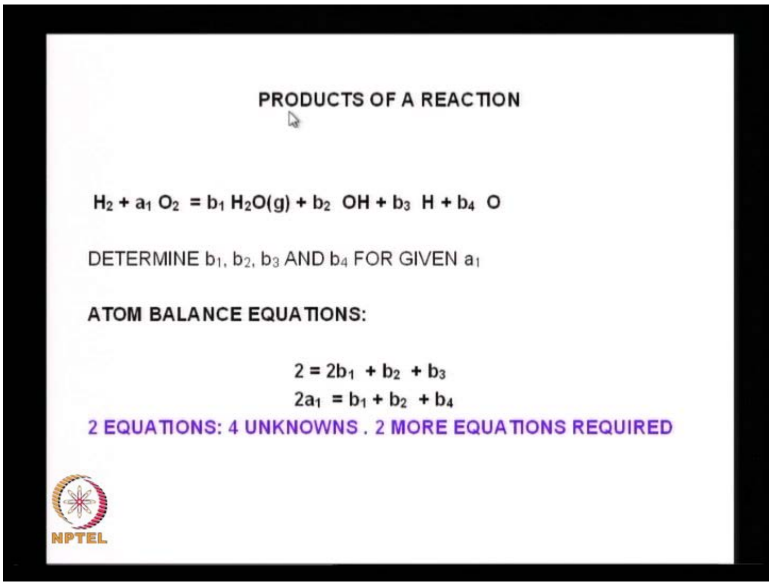

PRODUCTS OF A REACTION

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

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

In fact, I will come back to all this before I complete the the portion on chemical propellants'. But, let let us just go back and say, supposing I am interested in a products of a reaction. Like, let us say, I have the reaction of hydrogen and 1 mole of hydrogen with a1 moles of oxygen. Let us say, it gives me b 1 moles of water at a high temperature plus part of the water, is in which is dissociated into OH. Part is dissociated into H and part is dissociated into oxygen. Let us say, the temperature is going to be quiet high. I want to determine the temperature. To be able to determine the temperature, I need to determine the value of b 1, b 2, b 3 and b 4.

I also need the value of a 1? How do I get the value of a 1? We told ourselves in in rockets, we define fuel to or we define a term known as mixture ratio. What was mixture ratio? Yes, mass of oxidizer to mass of fuel. If we take this particular one, wherein I have a 1 moles of oxygen and I have 32 of a 1 that is, the mass of oxygen. Hydrogen is 2, which is equal to 16 a 1 and mixture ratio is specified. It could be Stoichiometry. Stoichiometry will be a8, if it is fuel rich.

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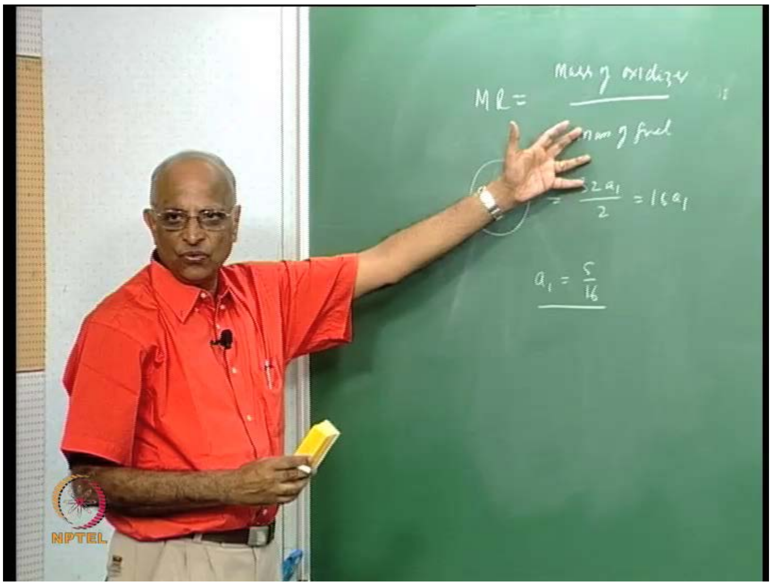

That is, where we want to operate our engine. It could be 4 or it could be 5. Let us say, I choose a value of 5. Therefore, I get a1 is equal to 5 by 16. That means, in any rocket, we must be told, what is the mass of oxidizer to the mass of fuel. Accordingly, I choose the value of a 1. Therefore, a 1 is known and what is it you have to find out. We have to find out in the products, what are the moles of b 1, b 2, b 3 and b 4. Therefore, we would like to find out for a given value of a 1.

Therefore, immediately, I say this problem is quiet simple. I know I have H 2 and I have O 2. Therefore, I have the atom balance equation. I have 2 of hydrogen and 2 of H and therefore, I have 2 b 1 plus b 2 here plus b 3. I also have 2 a 1 over here of oxygen and 2 of O atoms. Therefore, I have b 1 plus b 2 plus b 4 over here. I have these two equations which represents the atom balance equations.

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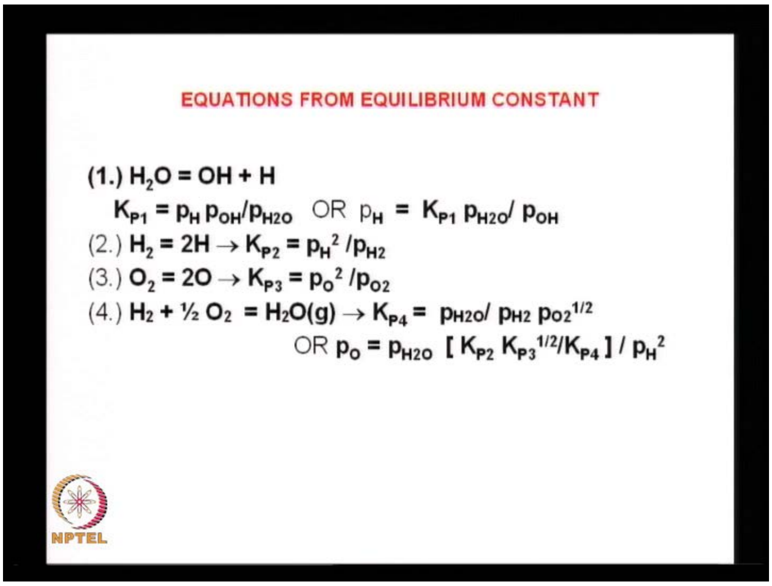

EQUATIONS FROM EQUILIBRIUM CONSTANT

(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.) $H_2 + ½\, O_2 = H_2O(g) \rightarrow K_{P4} = p_{H2O}/\, p_{H2}\, p_{O2}^{\,1/2}$

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

But now, I need to determine the value of b 1, b 2, b 3 and b 4. That means, I need four quantities and I have only two equations. Therefore, I need two more equations to be able to determine this value. Therefore, what are the equations I rely on? I say, that the the products are in equilibrium. That means, the net thing is in equilibrium. Therefore, I do a equilibrium analysis or a chemical equilibrium analysis. From chemical equilibrium, I say, well I can think in terms of water dissociating to OH and H or I can think of hydrogen dissociating into 2H. I can think of oxygen dissociating into 2 O or I can get H2 plus half O 2 to give me water again. Therefore, I use these four equations and for each of this equation, I write k P 1 is equal to P O H into ph divided by PH2 O. Or rather, I can write the value of PH in terms of kP1 into PH2 O divided by POH.

If I consider the reaction H2 going to 2 H, I have the equilibrium constant KP 2 as equal to P H square by PH2. If I consider O2 going to 2 O, k P 3, the equilibrium constant coming as P O square because, I have 2 O here. That is, PO square divided by PO 2. If I consider hydrogen and oxygen giving me steam over here, H2O as gas, I get k P equilibrium for this reaction as equal to PH2O divided by PH 2 and PO 2 to the power of half. That means, I use the value of these three equations and I solve for the value of P O and I get from from this equation, I get PO 2 is equal to under root k P 4 divided into into under root PH 2 divided by under root PH 2 O. Again, I substitute the value of, may be, P H 2 from here and I get the value of PO as equal to PH 2 O into KP 2, KP 3 half, KP 4 and PH square. In other words, using these three equations, I am able to get the value of PH in terms of PH 2 and POH.

I am able to get the PO in terms of PH2 O and P H square and PH, I already know in terms of POH. Therefore, instead of having four constituents, I reduce the value into two constituents, namely, the value of, may be PH 2 and POH. May be, you all should try it out. You know, you could need not necessarily take these these equations but, any any system of equations. All what we are doing is, we are trying to find out the partial pressure of hydrogen, in terms of water and OH. Similarly, partial pressure of oxygen in terms of H2O and OH again because, PH, I already know in terms of this. But then, what is it we get here? We get the value of partial pressure of hydrogen and partial pressure of oxygen. But, what I really want is the number of moles b 1, b 2, b 3 and b 4. How do I convert it to moles?

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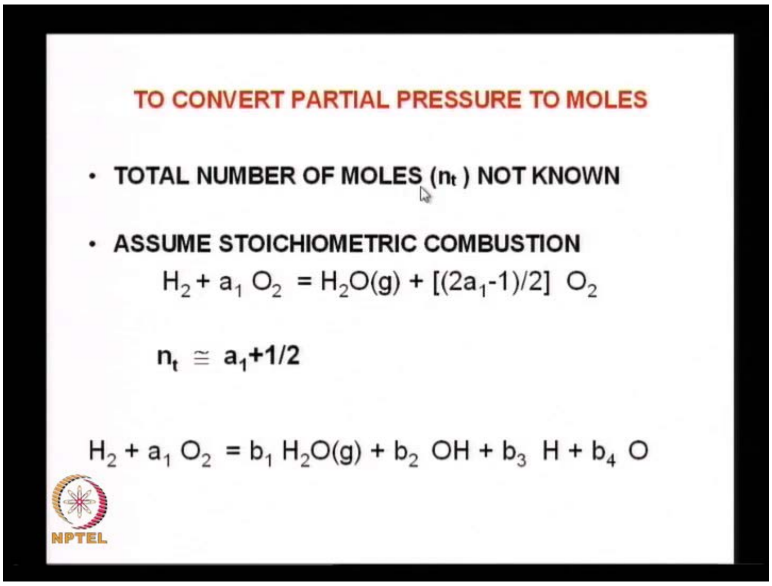

TO CONVERT PARTIAL PRESSURE TO MOLES

- TOTAL NUMBER OF MOLES (n_t) NOT KNOWN
- ASSUME STOICHIOMETRIC COMBUSTION

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

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

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

To covert partial pressure to moles, I need to know the total number of moles. Rather, let us do it on the board. If the total number of moles is, let us say, n T and the number of moles of H2O is H2O, then I say the number of moles H2O into into the total pressure is equal to the partial pressure of hydrogen.

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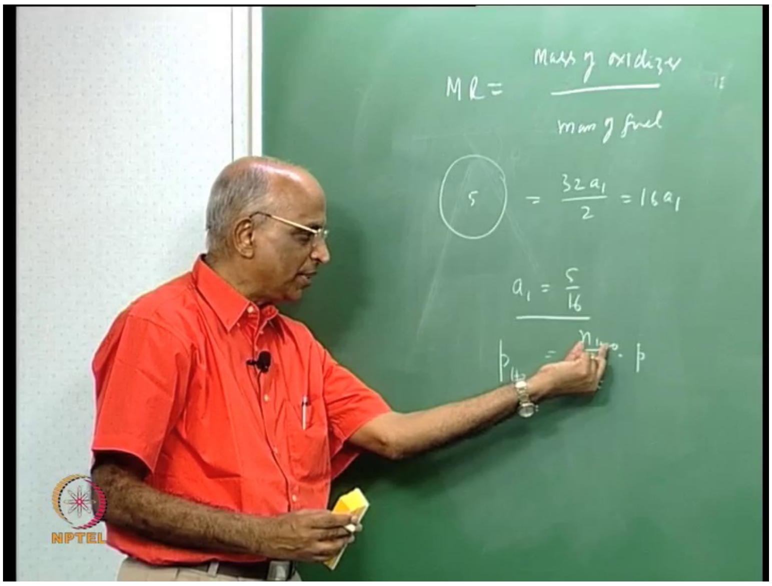

All what we are saying is the molar ratio. The total number of moles is n T. The moles of H2O is n H2O and therefore, PH2O depends on the total pressure into deep fraction of the molar concentration over here. That is what I do in the next one. Therefore, to convert, you need to know the total number of moles. But, we do not know the value of b 1, b 2, b 3 and b 4. But, how do I get it.

Well, let us assume Stoichiometry combustion. For Stoichiometry combustion means, we say the products of combustion form are complete. That means, I have H2O G and to get H2O G, I now get, if I have H2 plus a 1 oxygen is equal to H2OG plus I have balance of oxygen. Therefore, it gives me the total number of moles as equal to a 1 plus half. Then, I convert this into partial pressure of the products. Namely, I should be able to get b 1, b 2, b 3 and b 4. Maybe, I will continue this in the next class. I will just get started at this point in time. We will see how to get the number of moles of b 1, b 2, b 3 and b 4 and this will be an iterative process because, we are assuming something. We have to correct for it and this is what I will continue it in the next class. Well, thank you then.