Fundamentals Of Combustion (Part 1)
Dr. D. P. Mishra
Department of Aerospace Engineering
Indian Institute of Technology, Kanpur

Lecture – 18
Determination of chemical equilibrium composition

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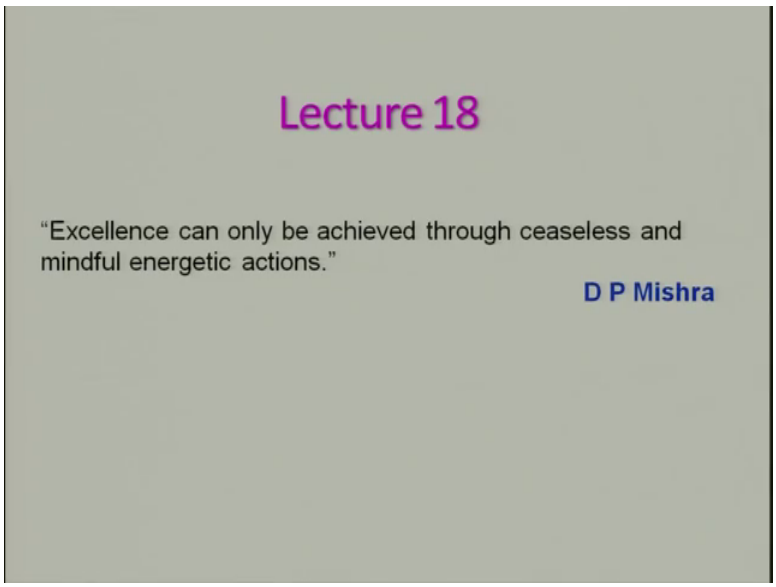

Let us start this lecture with a third process; excellence can only be achieved through ceaseless and mindful energetic actions. And in the last lecture we are talking about equilibrium compositions and how we will have to attain the equilibrium, which is important or life also. So, also for chemical equilibrium; what we did we took some examples now we today we will be looking at how systematically we can do right. So, can anybody re call how we can develop a procedure for determining equilibrium composition? Right in the in the previous example have given what is that?

One mole of o 2 is going to o, let us I will take a system methane and air right and I know let us I equivalence ratio 1 and let us say some temperature 1000 Kelvin, and atmospheric pressure one atmospheric pressure, then how I will find out equilibrium composition? What I will have to do, are you getting in the example?

What I took is very simple problem is given everything almost you can say, but here how we will do? That means, a question might be coming to your mind. So, what are the species which will be there at equilibrium, is that question coming to your mind or not?

See what are the what are the species will be there is it only CO 2 and water and nitrogen no certainly no there will be n number of species you know like you can say c s 3, c s, c s 2, c o h, o h, H water carbon dioxide, carbon monoxide, nitrogen n o x, like n o, n o 2I mean n number of thing right; that means, I will have to identify the certain species, which may be important for my calculation ok.

How to identify? Is an art and also; what is your requirement. Art means definitely you will have to choose let us say for methane system, carbon dioxide will have to choose yes or no we will have to choose water, we will have to choose nitrogen right for methane air system, there is no doubt about it I mean absolutely no doubt, but you will have to choose c o n n will actually and h, O H right H o 2 c s 3, c s 2 because c H 4 is there nah. So, therefore, these are things will be supposed to be there and there are several others species whatever you want you can you choose right; that means, first I will have to identify probable equilibrium species right ok.

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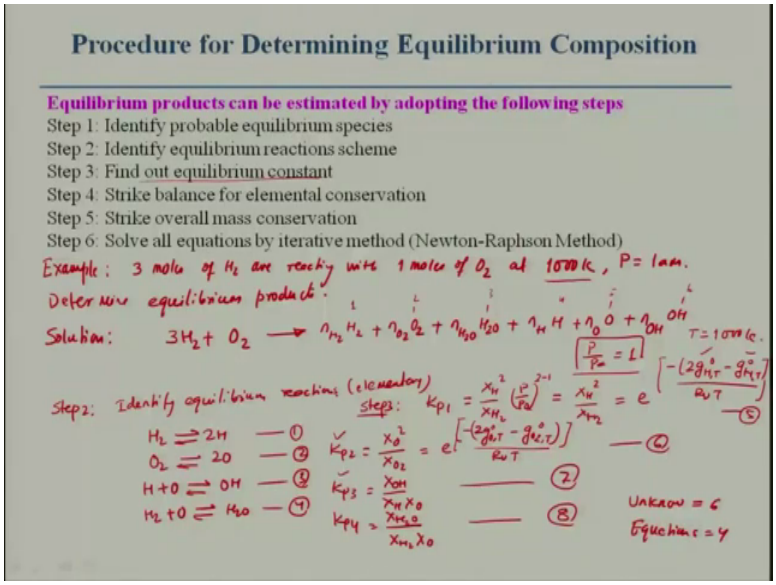

And then after identifying that, I will have to identify the equilibrium reactions schemes you know that is very important right. How to choose and other things also very important because whatever is known you will have to choose for which data is available you know for example, the Gibbs free energy then you will be choose. Then find out equilibrium constant right because I will have to find out what is that k p and strike a balance for elemental conservation right and strike overall mass conservation and then

solve all the equations you know by iterative method, you I can give example one example Newton Raphson method that might be several other numerical methods are available right.

The question might be coming to your mind why I will do that, because just now we solve a in the example which is a quadratic equation, you know very easy to do that right. If quadratic equation comes whether you will solve if it is an keep in mind that is only one equation right. So, therefore, you know quadratic equation do, and also it is non-linear right, but still you can solve that. Now to illustrate this point I will take an example right.

In this example three moles of hydrogen are reacting with one moles of oxygen at 1000 Kelvin and pressure one atmospheric; and what we will do determine equilibrium products right. So, if you look at what is happening? I am saying 3 moles of hydrogen reacting with 1 moles of oxygen going to the products right of course, what will be the products? What will be the products; that means, first I will have to step one is what step 1? If you look at step one is identify the specified the probable species at equilibrium. So, what are those species? Definitely n H 2 right, sorry, then H 2 right, then definitely will be oxygen then n water what else?

Student: (Refer Time: 06:36).

O or I can say H right n H n H right plus n o o plus n OH OH right let us say we will take this number of species let us say, I can take any more numbers also, but this case you know these are the probable OH is basically how many species are there. If you look at hydrogen is 1 right and this is 2 this is 3 H is 4, this is 5, this is 6 right ok. Now step 2 is what? Step 2 identify equilibrium reactions. So, when we are considering we will be considering what is the elementary reactions possible elementary reactions what do you mean by elementary reactions might be a question might be coming to your mind right? Where you know number of bond will be broken or formed is very less right, that we call it I will be discussing that little.

So, let us consider because we are getting H right and I can say that H 2 is going to 2H right similarly I can say O 2 2 can going to 2 O and H plus O going to OH and H 2 plus O going to H 2 O. So, this is basically equation 1, this is 2, this is 3, this is 4 right are

you getting so; that means, all species are coming here are not? H is coming, O is coming H 2 is coming, O 2 is coming total 4 and OH is coming 5.

And H 2 O total 6 species are involving in that; that means, I do not need any further chemical you know reaction to be consider for this finding out for equilibrium composition right and step 3 is what? You know like find out equilibrium constant. So, what we will do? We will basically find out equilibrium constants. So, for example, if I say for equation 1 I will say this is K p 1, for equation 1 I am saying K p 1 what it would be? It will be x I can write down X H square X H 2 this will be P by P naught what will be 2 minus 1 is not it. If you look at the formula I have derived for your arbitrary reactions right it will be you can use that or you can use it from the partial pressure and then convert that any one of them . So, in this example P is P is what?

One atmospheric pressure and this P naught or I can say this is P atmospheric pressure right; that means, this will be always 1, this will be always one in this example are you getting; that means, P by P a is 1 in this example is equal to X H square by X H 2 right can I not say 1 is equal to what? E right delta g H t naught divided by R u T. So, I can write down 2 g H right t naught minus this will be one. So, g H 2 t naught divided by R u T and these are known, I can get from the table corresponding to what? Corresponding to this temperature 1000 Kelvin that.

Means these values are known R u is known T is known right T is equal to 1000 Kelvin right and from table I can get these values ok. I will not do that right, but a I can get. So, let us say this is my equation 5; right similarly I can find out K p 2 will be X o 2 by x sorry x o o means atom o atom square divided by X o 2 is equal to similar way should I write down or let me write next I will not write down minus 2 g naught T oh I should be bracket minus g o 2 T naught similarly X p 3 X O H right by X H X O this I can say this is 6.

This is 7 because this will be known right this values is known this value will be I know these values. So, I know k p two similarly k p three is also known yes or no are you not getting K p 3 is nothing, but from the delta g naught T naught divided by R u T. So, I am getting this g of the species at particular temperature, from the table. So, therefore, K p 3 is known and K p 4 X H 2 O X H 2 X o yes or no. So, this your 8 now if you look at

basically 5 6 7 8 equations are there. So, total 4 equations how many unknowns unknown? 6 equation still now?

Student: (Refer Time: 13:54).

4; that means, I need to have two more equations to solve this thing yes or no right. So, then we will have to go for the step 4 we will have to go to the step 4 and step 5 to get another two equations right.

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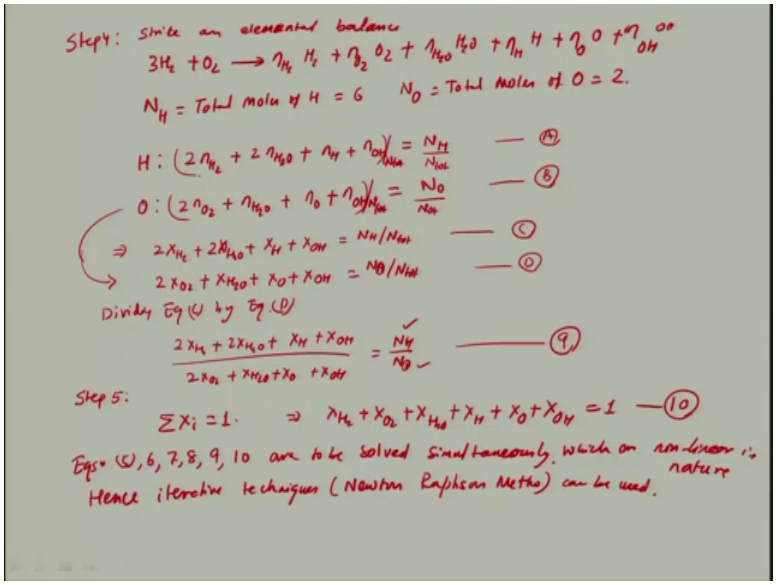

So, step 4 right is it step 4 strike an elemental balance right that elemental balance if you look at a moles of you know elements we will have to do, what are elements are involve in this reactions, what are the elements H and O right. So, let me write down also what we did that is 3 H 2 plus O 2 going to n H 2 H 2 plus n O 2 O 2 plus n water water plus n H H plus n o O plus n O H this is looks to be actually n this is n not eta and O H.

So, given if you look at what are the total number of H moles are given? NH if I say n H is the total moles of H is equal to what? 6 because 3 moles of hydrogen right. 6 and N O total moles of O is 3 is it 3 or 2 because one mole of oxygen right it is 2. So, we will have to do a elemental balance right. So, what I will do H what is that? If you look at right what I will be doing two n H 2 right 2, n H 2 right plus where is that here plus 2 n H 2 O because it is there right and then because left hand this is we are looking at the product side right and then this will be;

Student: n H.

N H only one is there then.

It will be n O H is equal to what? N H yes or no total number of moles in the product. So, it would be same as whatever there in the reactant similarly o I will get 2 n O 2 right and n water because this is 1 o in the product and this is 0 because there is no O and in this case it will be n O plus this will be n O H is equal to N O right let us say this is equation A this is B what I will say? I will just divide it right should I divide what I will get if I divide; that means, N H by NO I know then I will find it, but these are in the moles, but I need to express in terms of.

Student: Mole fraction

Mole fraction so that what I will have to do? I will have to divide this equation with N total, total number of moles right and if I divide by this all to together right N total similarly N total divided by N total what I will get? I will get 2 X H 2 plus 2 X water plus X H plus X O H is equal to N H by N total. Similarly from this expression I can get two X O 2 plus X water plus X O plus X OH is equal to N H by N total. If I say this is C and D. Now I will divide C by right dividing equation C by equation D we will get what is that? 2 X H 2 plus 2 X H 2 plus x H plus X O H divided by 2 X O 2 X plus X O plus X O H is equal to N H by this will be NO there is error here NO in equation D NO and total cancel it out, this will be equation 9 now, right.

Because this is known N H is known or not; NO is known. So, therefore, I mean these are unknown and we will have to evaluate, and what I will have to do now step 5 right close the equation basically we will have to a balance what is that summation of mole fraction equal to 1 right because these are 5 equations and 6 unknowns. So, we will have to close that equation for that we will have to do this, and this is equal to X H 2 plus X O 2 plus X water plus X H, X O plus X O H is equal to 1 this is 10; that means, if you look at right this equations has to be solved like equation equations what is that 5 6 7 8 9 and 10 are to be solved simultaneously right see if it is linear equation you know how to solve ok.

But if it is non-linear equation it will be difficult. Why it is non-linear equation can anybody tell me why? You will have to go back to the equation 5 and 6 see if you look at

this is X H square X O square right and X H X O right . So, therefore, these are non-linear.

So, for that solve right this equations are non-linear in nature non-linear in nature, hence iterative techniques right iterative techniques like numerical methods can be used and the one is you can say Newton Raphson method can be used right. So, if you look at it is not that easy to really do, this you are talking about if the temperature is known and the equivalence ratio or the fuller ratio is known, then you are finding out compositions right. Now you imagine in adiabatic temperature is not known temperature is not known, when you are talking about fuller mixture you do know the temperature you do not know, now how we will have to get this composition? These are all in telling because the temperature is dependent on.

Student: (Refer Time: 23:20).

On this composition why? Because Gibbs free energy is dependent on the temperature and this Gibbs free energy is that k p values will be different, because Gibbs free energy is different. So, k p values will be different. So, therefore, the composition will be different are you getting.

Student: Yes sir.

Now, you will have to do that, how we will do it is a very difficult thing and then we will have to do iteratively now we are going to see how we are going to do that.

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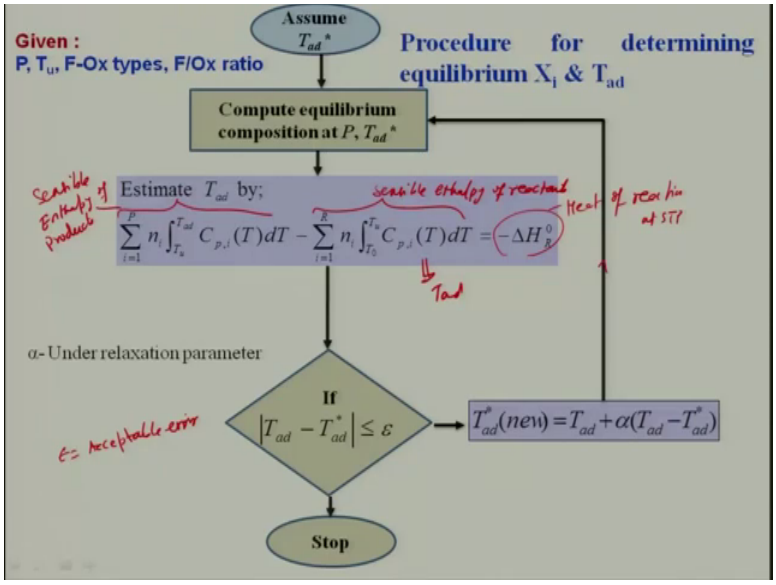

We will have to determine how to device a procedure for determining equilibrium compositions; that means, mole fraction of species and also there will (Refer Time: 23:57) both are intellect. So, I will just tell you the procedure give in that, pressure is will be given and the unbound temperature is given. It need not to be 298 Kelvin it may be 600, it may be 500 whatever it may be right it may be 298 Kelvin and fuel oxygens types whether it is hydrogen air methane air or propane air or propane oxygen or kerosene oxygen you know like that is to be also known otherwise you cannot do and what is the fuel oxidizer ratio has to be given is that clear?

Theses has to be given now what we will do? We will have to assume a adiabatic temperature, because we have already seen in the last procedure that temperature should be known then only I can find out composition. So, I will assume a t a adiabatic temperature. Then compute the equilibrium composition at a particular pressure and a adiabatic temperature that we have already seen how we will have to do that iteratively that is also iterative this is a iteration inside iteration you know we will have to do that now.

So, then what you will do? You will estimate the adiabatic temperature by this is your sensible enthalpy right this is your sensible enthalpy of the product, and this is the sensible enthalpy of the reactant are you getting of reactants. This is your sensible enthalpy of product. Product involving various species n i will be you know various species it can be you know if it is product it will be if I take consider methane, that might be twenty species or the ten species at least you know 15 species kind of things right.

So, now, and if it is a reactant of course, it will be methane air only methane oxygen nitrogen right reactant will be easier to handle, but product will be several of them. Now once you this thing because you have already find out composition; that means, you know this n I right or in terms of moles fractions, then you can do very easily and this is nothing, but your heat of reaction this is heat of reactions at STP right. And then by this you will find out T adiabatic because we will have to integrate keep in mind this.

C p is a function of temperature right that you will have to plug in and then integrate that integration is not that easy the way we did example is not the way there you will have to integrate because the the various temperature range, you will have to use different C p values at so on that I think right and then you will have to find out.

Now if this T adiabatic right whatever you calculate right this is the calculated one calculated from here from these you will get T adiabatic and minus T adiabatic gets, let us say you gets something 2000 Kelvin now we are getting 2400 let us say; that means, this is not acceptable. If it is small values let us say 1 percent error right then you will say accept. Let us say if it is the assume value is 2400, but the accu the calculated value is 2410 Kelvin, then we are fine because this is you can you need not to go again it will be stopped. Otherwise what we will have to do? We will have to find out a new adiabatic temperature that is equal to T adiabatic, alpha into T adiabatic minus T adiabatic right.

And these alpha is basically the under relaxation parameter then you will go back to here and again calculate right the because it is the new adiabatic temperature, then again compute the composition again go through this all this process till you get this error this error your error this error is the acceptable error right as I told it is one percent you are happy fine. If you are happy with the 0.0 0.5 percent, right we will have to go on doing that; that means, it is iteration in between iteration this is a quite complex are you getting to the point?

Student: Yes.

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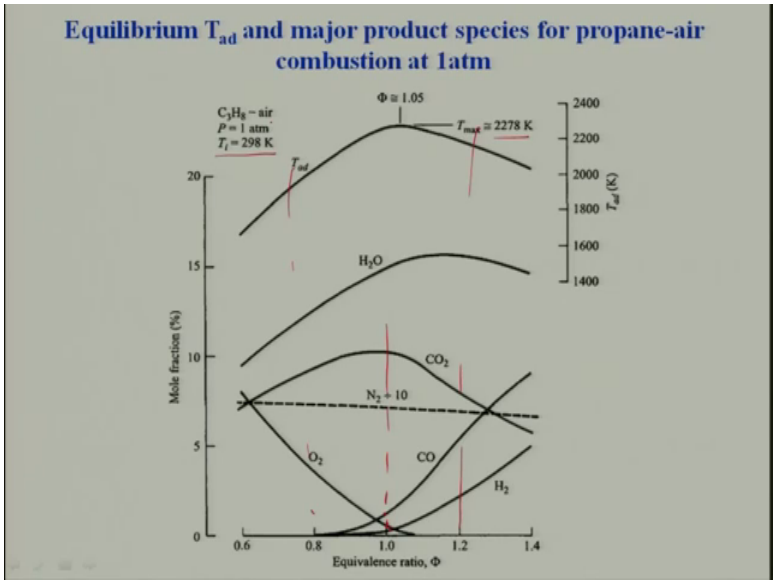

Ok. So, now, let us look at you know if you do this calculation for a methane propane air system at different equivalence ratio you will get different things right.

For example, equivalence ratio one you will get you know water here and then C O 2 this label if I take this one right and of course, nitrogen divided by this not changing much right you will get CO value is here and oxygen here hydrogen here right even if you one at different this side you will get different values, similarly you will get different values you know like keep in mind that this corresponding to adiabatic temperature, you are getting maximum temperature you will get 2278 Kelvin, phi is equal to 1.05 and this corresponding to 298 Kelvin and one atmospheric pressure. And these are all measure species these are all measure species not ridicules under the things.

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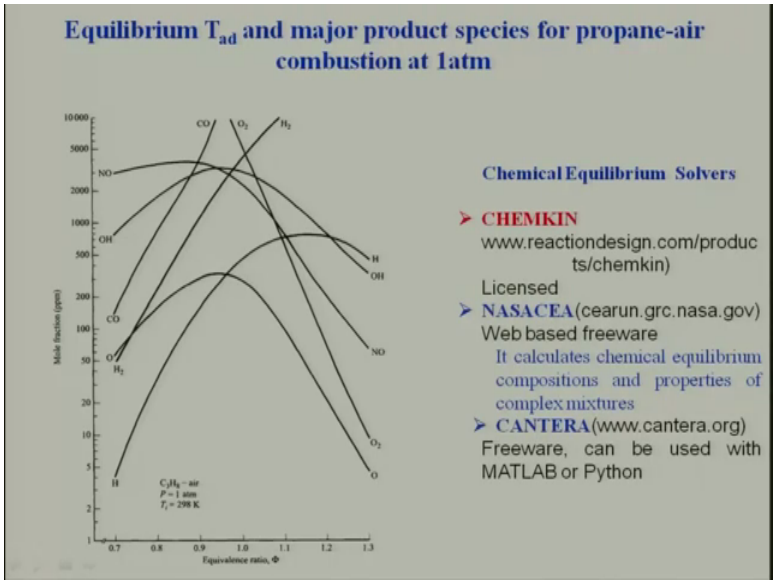

So, we will be now seeing if you do this thing you will get various values like you know hydrogen O H O NO O values all those values you will get. Now for that you can use you know several softwares which are available like Chemkin Nasacea and Cantera and I was told this Nasacea is a basically is a free softwares these are all you will have to by Chemkin and Cantera is all free where you can use matlab python kind of things. You know it is a plugging you can plug in the thing you do programming. If there are several other softwares are also available in internet, it is explore and find out so, that we can you know use this thing, right.

Thank you very much.