Indian Institute of technology Madras

NPTEL
National Programme on Technology Enhanced Learning

COMPUSTION

Lecture 4
Dissociation of Products, Role of Pressure

Prof. S R Chakravarthy
Dept. of Aerospace Engineering IIT Madras

What we did last time I had given some example values for these heats of formation made a mistake there is not supposed to a decimal place it is supposed to be a comma that means you are off by about three orders magnitude and what we said is last time okay. So I wanted were talking about this equation that is used to find the adiabatic flame temperature and the point I was trying to make there is if you want to have a fairly high adiabatic flame temperature for the for the products which is given by having this ni'' over here then what is given to us is ni' and T1 and maybe the pressure that is given to us which will determine ni'' in a way that we will see okay. But effectively what is happening is if you now have a t1 let us suppose that is significantly low could be 298 Kelvin or maybe 500 Kelvin or 700 Kelvin.

But it is not supposed to be it is not expected normally to be something like the aerobatic flame temperature itself, so effectively the sensible enthalpy of the fuel is going to be low because the temperature is the initial temperature is low okay if you want to now have a high value for this that means you want to have a high sensible enthalpy for the products that means we want to have a high negative value of the heats of formation standard heats of formation for the products okay.

So those are the ones that actually give you stable products you get stable products mainly when the products are having high negative heats of formation yeah and then this total will be such that you get a fairly high sensible enthalpy for the products and therefore the adiabatic flame temperature, but if the total itself has to be high then given that the sensible enthalpy of the reactants is low and let us say that one of the reactants is oxygen which is like a reference element therefore the eats of for heat of formation standard a deformation for that is zero we are looking for this total to be high only by looking at the heat of formation under standard heat of formation of the fuel okay.

That means we want to have the standard heat of formation of the fuel to be high okay, or in other words you look for a substance which has a high standard heat of formation then you can identify that as a field that is a way we basically look at it right. So if you look at typical values of the heats of formation standard heats of formation for typical fuels let us say I have listed here taking the taking the source from a sort turns book let us say we have methane a setline ethane and propane and propane right so again keep on going to higher and higher hydrocarbons we see that some of them are negative some of them are positive okay but what we are looking for is essentially that even if they are negative they should not be high negative values okay.

So it could be somewhere around 0 negative or positive, positive is better but we do not want them to be as high negative values as the the product standard heats of formation. So that we will get some high temperatures there okay, so this is how you are essentially looking for identifying the fuel this is one point that I wanted to make. The second point I wanted to make today is by actually looking at it this way we are constructing a hypothetical set of reactions that do not exist in reality but it is actually somewhat in our minds for a thermodynamic convenience because thermodynamics we are dealing with enthalpies here we recognize that these heats are all enthalpy s and these are state variables right.

So it is sufficient for us to actually go from one state to the other okay, so the way we are doing this in decomposing the enthalpy of the reactants into the standard heat of formation and the sensible enthalpy and we are also decomposing the enthalpy of the products into their standard heats of formation and they are sensible entities that is what we have done right. So what is essentially going on is you are starting with a set of reactants which are at some temperature and pressure okay.

So we watch you of being at some temperature they are having a certain sensible enthalpy which is nonzero okay, by looking at this kind of thing what we are doing is we are now bringing the reactants from their given initial temperature to the standard condition by which let us say we now takeaway some heat okay and cool this and we now bring it to the standard state. So we now supply the heat of formation the standard heat of formation to these reactants at the standard condition all right and go through reverse formation reactions to make the reactants unwrap their bonds and give rise to reference elements.

So you now have reference elements at standard state okay, and you now have the reaction go happen that is do you now have reference elements these reference elements now regroup themselves to form the products at standard state thereby releasing the standard heat of formation for the products. And finally we still have in this budget okay, we still have some heat that is that is available to us which will which will be used to raise the sensible enthalpy of the products from the standard state to wherever it can go so that it can you heat used up all the heat that is available okay.

So the most of the heat was actually available to us in this process when you now try to actually form the products you got a lot of heat okay that heat has to simply and then you have supplied some heat to actually unwrap the bonds of the reactants to the standard state, so you have to you have negated that okay you got some heat by getting the reactants from their initial temperature down to the standard condition let us suppose that the reactants were heated up to 500 K okay there is already some sensible enthalpy available with them which was been which could be taken into account when trying to bring them down hypothetically to the standard condition right keep that heat with you supply some heat for unwrapping the bonds to get the reference elements and then get the reference elements to form the products you get a lot of heat over here a little bit of heat over here you have supplied some heat over there all that stuff.

Now will add up to some net heat that is available to you which you now dump on the products to raise the temperature all the way to the adiabatic flame temperature which over temperature they can go to okay. So it is like a circuit is path it determinably speaking that we are taking for the reactants from their state to their standard state and then you form the standard the reference elements from the reactants and use the reference elements to form the products and then raise the temperature of the products to the to the whatever okay.

So this is the circuit a spot that we are having in our minds while we are doing this okay, yes this has got to do with the way the bonds are in there okay so we have like some of them are saturated bond some of them are unsaturated and so on, so that is something that we would not get into in this in this class okay this is like there is a thin line that are separating us from chemistry itself okay. So we don't we would not get into that but the point I am trying to make is the numbers okay, this are not supposed to be as high negative values okay. So it is okay if they are negative values but they should not be very high negative values okay and if they are zero or positive better okay as high as possible that is algebraically high is what we are looking for.

And the other point I wanted to make is so you know in all these things we have actually said that is the K adiabatic process that is going on that means you are not simply getting any heat at all right, does it make sense? When I burnt stuff I get heater what are we talking about adiabatic?

So it is not as if I am trying to say that this is an ideal thing and in reality there is some heat loss so it is not adiabatic and all that stuff, no in reality you are not very far away from the situation for most applications okay in the core of the combustion process in let us say in a rocket engine or a gas turbine engine or whatever it is you get temperatures that are pretty close to the adiabatic flame temperature within let us say a 100^0 or something all right we just be just not a lot of deviation when you are looking at something like 2,500 right.

So we are not talking about a heat loss as a non adiabatic situation the point we are trying to look for is most of the time when you are looking at the heat that is generated in the combustion right, we are primarily looking at the hot products that could be used the heat in the high temperature of the hot products that could be used okay. So we are now looking at something like a steam turbine where you are actually essentially having a high temperature steam that turns the wheels right your counting on the high temperature of the steam to the thermal energy that is associated with a high temperature to the steam to be important into the turbine blades.

Similarly for the hot combustion products by virtue of the fact that they have high temperature is what we are trying to utilize, so we just put a kettle on a star okay what is actually heating the kettle is the hot products it is not the chemical reactions itself the chemical reactions are over many millimeters below will be below the kettle okay the flame itself is not really near the kettle at all okay the flame is it the flame were to happen near the kettle the flame will get quenched and it will become non adiabatic but the flame is actually on the stall again it is on the burner and you get these hot products and the hot products are the ones that are actually flowing around the kettle and heating up the kitten right.

So the question basically then is what is the heat that you are going to get out of a chemical reaction or other words you know now looking at these fields with heats of formation and so on maybe in lots of practical applications as well as in your high school or wherever you have learnt any combustion you would have come across things like heating value of the fuel okay, you are a calorific value of the fuel and so on.

So when I now have a fuel in hand can I can you tell me how much it is going to how much heat it is going to give okay do not tell me all these things like the circuit is over which it's going through and then heats of formation transaction reference elements and all these things that is not too confusing okay is it possible for me to see the calorific value or the heating value of the fuel from this can we? Can we? You can it is all embedded in here right.

So what we are looking for is if you now do not really bother too much just for the sake of approximate argument okay if you did not bother about the fact that the reactants and the products had different CPE the molecular weights and so on right, so you are just simply looking at sensible enthalpies you are simply saying I had a bunch of reactants at a let us say room temperature or initial temperature t1 okay and so that means the sensible enthalpy you if that was pretty low and I had to now get have this feel release heat that will increase the sensible enthalpy of the of what were reactants to start with to a very high sensible enthalpy value for the products okay.

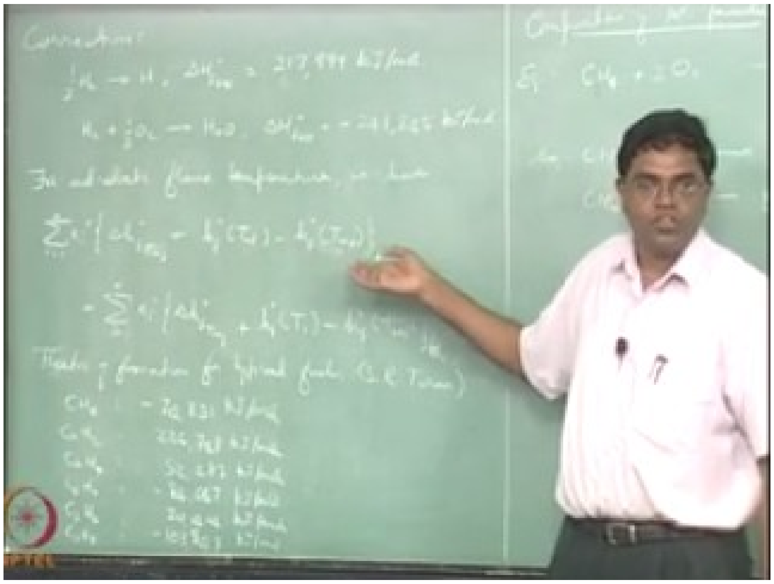
So the heating of the heating value of the fuel is primarily going into changing the sensible enthalpy of whatever reactants to what was what will be products, so essentially that is what is going on. So if you now look at then this part minus this part that is a sensible enthalpy change that is being affected okay.

If you now take that to one side okay and keep this part on this part to the other side then it becomes automatically that the difference in the standard heats of formation weighted by the individual track a metric coefficients of the products and the reactants is effectively the heating value okay or in other words the heat that is actually released during chemical reactions in the combustion primarily comes from a difference of the heats of formation weighted by the amounts by which they are this is basically what's going on okay and it comes to directly from here okay.

So finally the last point that I want to make here is this essentially says that all of combustion is all about a transaction between heats of formation and sensible enthalpy we started out with substances reactants which were low in sensible enthalpy high in heat of formation okay, we now finally get to products which are high in sensible enthalpy and low in heat of formation. So essentially it is like what you started out with low sensible enthalpy high heat of formation gets transformed into the other combination okay. This is exactly what is going on in remaining this adiabatic flame temperature okay.

So now let us look at the question that I post towards the end of last class which is where is the pressure showing up here right it is supposed to be a constant pressure process where is the pressure showing up here is really the question right. So the answer to that is sitting in this ni’’ or the pressure is possibly the one that's going to dictate what should be the composition of the products is what we expect okay, the question is how okay.

(Refer Slide Time: 15:53)



So the next point that we have to look at is composition perhaps we will start with a very simple example which is going to be puzzling to us in a minute right, so example let us suppose that we consider a reaction where you have ch4 + O 2 gives co2 + h2o okay, can we figure out first of all how many species are therein this system four species the capital N here is four right how many well I should not ask the next question now.

So can we now figure out let us suppose that we had one mole of methane okay and then we will do what's called as balancing the reaction right so you know how one carbon atom here one carbon atom here that is fine and then we have like four hydrogen atoms here it will give you only two so we get two moles of water there and then we have like 2 oxygen atoms here and then 2 there we have only 2 so we have this is supposed to be a stoichiometric reaction.

So this is what we this is what we expect now here it is pretty clear, the composition of the products is just as clear as the composition of the reactants okay this is this a stoichiometric structure metric right so ch4 + o2 will be fuel rich because here we are starving the system of 1 mole of oxygen and ch4 + let us say 3 o2 is feeling right. And correspondingly we should now be able to put in let us suppose that some excess in the case of fuel rich we now suspect that there must be some excess amount of methane that is remaining as products and in the case of fuel lean there is like some excess amount of oxygen that's remaining the products we should be able to find out yeah.

So for example we now have ch4 + 3 o2 whereas one mole of ch4 is going to consume only two moles of oxygen there will be one mole there is excess okay and if there is one mole that is excess, what is going to happen to the adiabatic flame temperature, why? Why would the adiabatic flame temperature decrease if you now had a excess amount of reactant that is off stoichiometric condition.

The answer is you are now actually soaking up so much amount of sensible enthalpy for the excess reactant that is remaining for it to be also taken to the adiabatic flame temperature you see therefore you are not going to reach a very high adiabatic flame temperature it is sort of like you now have this excess reactant that is remaining there which wants to share the π on what is available for the sensible enthalpy rice okay.

So yeah I am going to rise a lot whereas if you do not have any excess okay, it is only the these products they need the stoichiometric products that are remaining then they are the only ones that are going to actually go high up in the innocent you need the sensible enthalpy therefore they can actually reach fairly high temperature, so what it means basically is near the stoichiometric condition I am not saying at okay.

And let me qualify that a little bit near the stoichiometric condition is where we can expect to have the highest adiabatic flame temperature okay off stoichiometric conditions the rebar a flame temperature drops because you are having excess of one of those reactants that also needs to be heated up to the adiabatic flame temperature therefore you do not get up to that high in adiabatic flame temperature as you would without the excess reactant right okay.

So why near instead of at it is got to do with how you look at the sensible enthalpy recall that we could look at the sensible enthalpy as an integral CP DT or if you're thinking caloric feel calorific ally perfect gas which is which is simpler it is like simply CP times T adiabatic minus TT difference right. So it now matters on what is the CP of your reactant okay so typically you will have and the CP will depend on the molecular weight okay and typically we expect that the fuels will have lighter molecular weight when compared oxidizer and therefore a higher CP and so if it can actually hold more heat it is going to decrease the temperature because the CP is now holding the heat and not allowing for the temperature to rise okay.

So that is going to send you if you are now looking at how the adiabatic flame temperature is going to vary as a function of fuel ratio okay you are going to actually have a peak that is slightly away from the stoichiometric value because the SI piece of fuel and oxidizer or and the reactants they will be different, so you have to worked it out okay. The other thing that you can also think about is in this reaction we are only looking at o2 but in reality it could be air which means you have a lot of nitrogen involved right.

So you now have nitrogen which does not participate in the reactions the means it shows up on either side of this reaction okay what is the consequence of the presence of nitrogen for the adiabatic flame temperature relative to if you did not have the nitrogen obviously you are going to have much less adiabatic flame temperature because the nitrogen is now sitting there soaking up the heat okay.

So it is now going to contribute to the sensible enthalpy component as well so when you now have a total amount of sensible enthalpy that's available for you to increase the temperature the nitrogen also comes in for its share and therefore you do not get a very heightened high since Philadelphia keep in mind the nitrogen has a CP which corresponds to a diatomic molecule okay.

So instead of nitrogen if you had let us say organ alright which is a monatomic molecule it is CP is different because CP typically depends on for gases particularly on the atomic city of the molecule okay mono atomic diatomic polyatomic and so on okay, when it is polyatomic whether it is linear or is it nonlinear and so on right so depends on whether you have rotational degrees of freedom that needs to be considered right.

So if you now replace the nitrogen by organ then you will now find that the way the diluents say I think effectively nitrogen as well as organ was acting like a diluents and the diluents now going to the mono atomic nature or the dynamic nature of the diluents is going to change the way that the adiabatic flame temperature comes down and even within a monatomic if you now try to replace organ by helium yeah.

So organ has a higher molecular weight helium has a lower molecular weight correspondingly the CP changes right soon per unit mass basis and then if you now calculate things on a per unit mass basis then you will again see differences. So I would like you to work out those kinds of details like for example in an exam we can directly ask you if I now replace so much amount of nitrogen by so much I want of organ what is going to happen to the adiabatic flame temperature increase or decrease okay, so we should be able to figure that out okay.

So those are things that we can look at what we were talking about is the composition of the products and as I was pointing out if you have a stoichiometric mixture where you have considered these two as the stable products finally you now know exactly what the composition is if you are now looking at off stoichiometric situation you could still expect one of the reactants to be in excess and find out what it is or how much it is exists right in which case you still know what the composition of the final products are including the excess reactant that was on the product side okay.

So where is the problem? We could find out the composition of the products we know what they ni’’ is the pressure does not did come into picture at all is there a problem or does not the adiabatic flame temperature does not depend on the pressure at all right because we you might expect because it is based in enthalpy stand for ideal gases we showed that enthalpy is only a function of temperature it is just a balance of enthalpies okay, constant pressure yeah we are balancing enthalpies therefore constant pressure otherwise it does not matter.

So pressure does not come into picture at all that is not quite true okay, in reality you know now we have to look at reality okay, in reality these are not the only products that happen these are the products that we would like to keep okay, these are the products that we would will be expecting as the stable products.

But imagine when you now have these, these are the final stable products and keep in mind that these are the final stable products that means they have the highest negative heats of formation which is now going to give rise to an estimate of a very high adiabatic flame temperature that is to say if in case they were the only wants to exist you are now going to have a high enough adiabatic flame temperature that is now bringing, that is now going to cause a decomposition of these right.

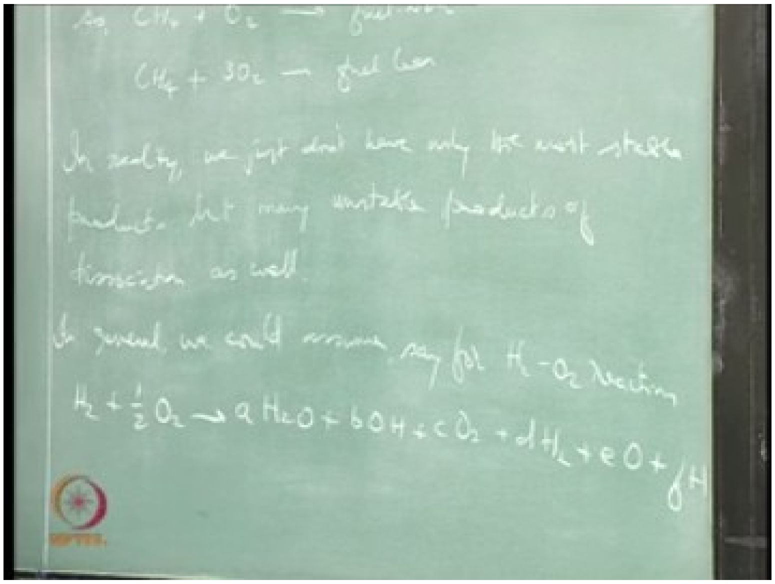
They just cannot exist at those temperatures the way they are okay, so H_2O could now did not get decomposed into OH and H for example right, and that decomposition is going to soak up some energy and decrease the adiabatic flame temperature that is one, one problem as far as the T adiabatic is concerned but the other big problem that we are talking about this how much H, how much OH. If I now have to factor in that you need to have some H and OH is also thrown in there okay, how much H how much OH because I need to know that, otherwise I would not know first of all it increases the number of species right, total number of species.

The second thing is what is the Ni″ for those and if now going to bring in those this is going to change, so pretty much everything changes right. So how do we bring the existence of those kinds of ions or radicals in there okay, as decomposition products of the stable products what we then assume next okay, is that let us suppose to be started out with reactants and they give so then it could go through this fictitious part and all that stuff that we talked about you are now looking at the final state.

The final state of adiabatic flame temperature is such that these products are in equilibrium with their dissociation products, okay. So if you now have H_2O okay, it could be an equilibrium with Oh and H right, so if CO_2 where to decompose it could be in equilibrium with its decomposition products. Again we do not know exactly what would be the nature of those decomposition reactions right, there could be multiple ways by which these decomposition reactions could happen.

So the simplest way again is for us to hypothetically assume formation equilibria that means if you now look at many more species of these unstable, many more unstable species to be considered right, we now have to actually consider their formation reactions as the equilibria equilibrium reactions okay. So let us just go through that a little bit more so in reality.

(Refer Slide Time: 29:24)



As, $CH_4 + O_2 \rightarrow$ fuel-rich

$CH_4 + 3O_2 \rightarrow$ fuel lean

In reality, we just don't have only the most stable product but many unstable products of dissociation as well.

In general, we could assume, say for H_2-O_2 reaction

$H_2 + \frac{1}{2}O_2 \rightarrow aH_2O + bOH + cO_2 + dH_2 + eO + fH$

Reality we just do not have only the most stable products but many unstable products of dissociation right, as well okay. So in general we could assume say for the H_2O_2 reaction right, H_2O_2 reaction if you now say H_2+1/2O_2 we have strictly speaking if I were to look at only this stable most stable product here sure it has to H_2O okay, so what I would actually have to say is I have only and I would like to say it is only one mole so that means I know a=1 yeah.

But in reality we have to now consider bOH+CO_2+dH_2+eO+fH alright, now what happens here is because this is stoichiometric okay, we want to expecting either O_2 or H_2 okay, if it R stoichiometric let us say if it is fuel lean right you could expect some O_2 if it is fuel rich we could expect some H_2 that is what we were thinking before.

But now what is happening is you could have H_2O decompose into OH and H but H could combine to form H_2 okay, and you could also have O atoms come up okay, during this decomposition which can recombine to form O_2 so you now have a soup bowl of lots of things that we did not really bargain for all right and all these things are there, so how do you handle them okay, so effectively we now need to have one two three four five six unknowns that we need to work out okay.

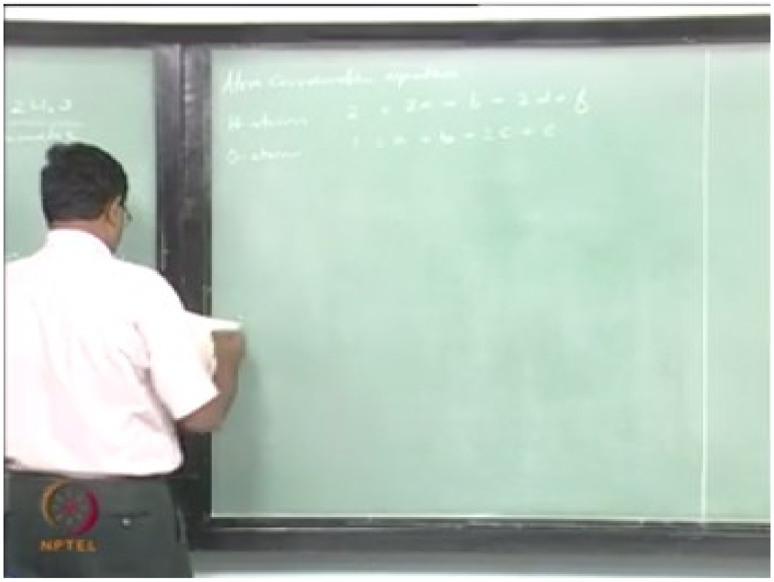
So previously how many unknowns did we actually work out by balancing the reactions we worked out about two or three okay, two here if one of them were excess we would just be able to handle that as well, how did we do that, how did we actually end up finding out the decomposition of the products by what is called as balancing okay, what were we doing when we were balancing. We were actually looking at the counting of the number of atoms of a particular type okay, so what did I do I said I have one carbon atom here I have one carbon atom here through four hydrogen atoms here but only two therefore I put a two there and so on right.

So it was essentially looking at a particular atom type and I was balancing the number of atoms this is the hallmark of chemical reactions, because chemical reactions are all about exchanges only at the electron level and not at the nuclei level okay, and what you are looking for say mass balance in a chemical reaction mass is conserved it is the nuclei mass that you are looking at okay, so we are actually mentally writing what is called as atom conservation equations for each atom okay.

And you can only write as many atom conservation equations as the number of atom types that are there in the system okay, so in the case, so to give an example so in the case of CH_4+O_2 how many atom types are there three okay, we have carbon, hydrogen, oxygen so you know we can call this a C - H – O system okay CHO system okay. In the case of the H_2O_2 system how many atom types are there only two okay, so if you now were to write atom conservation equations for these okay in an attempt to balance the reaction we would get two equations.

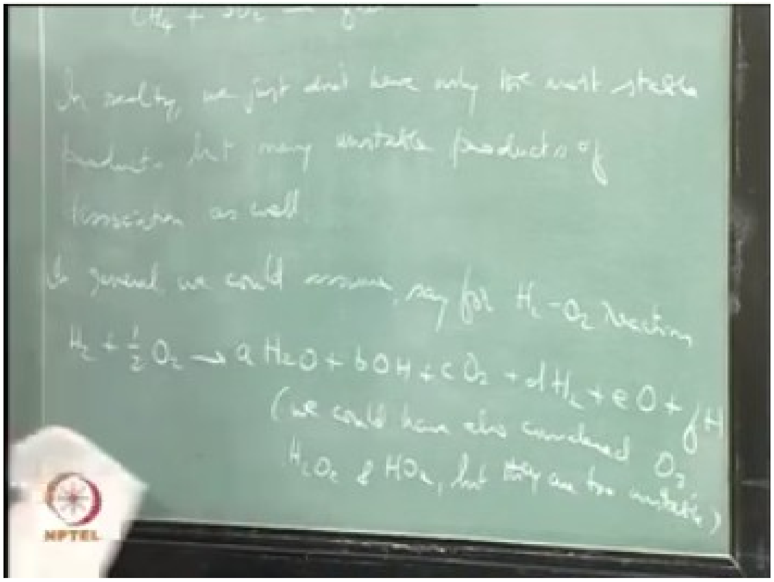
But we still are actually having six unknowns that means there are four more unknowns for which we need to develop equations right, so let us first do what we can which is atom conservation.

(Refer Slide Time: 34:28)



Atom conservation equations which is on the left hand side for H atoms we can write 2 that is given to us okay, so 2= we have 2a+b+2d+f basically looking at wherever hydrogen shows up and for O atoms we have 1=a+b+2c+e okay, I want to note here that we could have also considered.

(Refer Slide Time: 35:30)



In reality, we just don't have only the most stable products but many unstable products of dissociation as well.

In general we could assume, say for H_2-O_2 reaction

$$H_2 + \frac{1}{2}O_2 \rightarrow a\,H_2O + b\,OH + c\,O_2 + d\,H_2 + e\,O + f\,H$$

(we could have also considered O_3 H_2O_2 & HO_2, but they are too unstable)

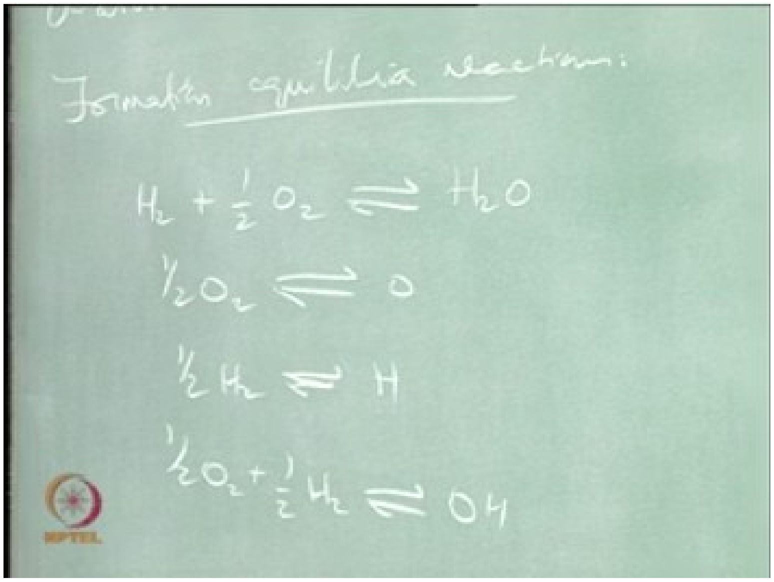
O3 ozone yeah, H_2O_2 and there is nitrous on stable species called HO2 okay, but they are two unstable okay, if you want to consider them that means we will have nine species okay, and then we are still stuck with only two atom conservation equations that means we now have to develop seven more equations rigt, and what we expect to find is these will be in very trace quantities that means if you now had after H if you had DH and I for these DH and I values will be very small is what we are expecting okay, therefore we are neglecting this. So what is happening now is the final answer for the adiabatic flame temperature actually depends on how many products you are willing to consider.

If you were to consider only two products you will have a fairly high estimate of the T adiabatic okay, if you want to have realistic estimates that means you have to consider more products, how many more depends on how cumbersome you want to get yourself into right, so we want to be reasonable that means we neglect some most unstable species. But we have to consider some less unstable species also in the picture okay, so and then we have to now look at equations for these.

So what did I say we now consider hypothetical formation equilibria for the other ones right, so effectively what basically happens is you now look at OH, O and H for example and H_2O okay, these are ones that are not reference elements H_2 and O_2 or reference elements so in your mind you should be essentially looking at these two equations actually serving the cost of O_2 and H_2 which is the reference elements for the two atoms, atom types that we are looking at that means for every reference element that is there as part of the products okay, it corresponds to a certain atom and the atom conservation equation for it is essentially tacked to its coefficient is like mental note it is all of them are coupled together it is like it is difficult for you to say this equation belongs to that and so on.

But for us to a number or what you call enumerate the number of equations that we have effectively any product that is not a reference element is what we will be writing the hypothetical formation equilibria based on the reference elements okay. So then you will get the additional equations so that is what you are going to do now which is equilibrium formation equilibria reactions right.

(Refer Slide Time: 38:37)



Formation equilibria reactions:

$$H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O$$

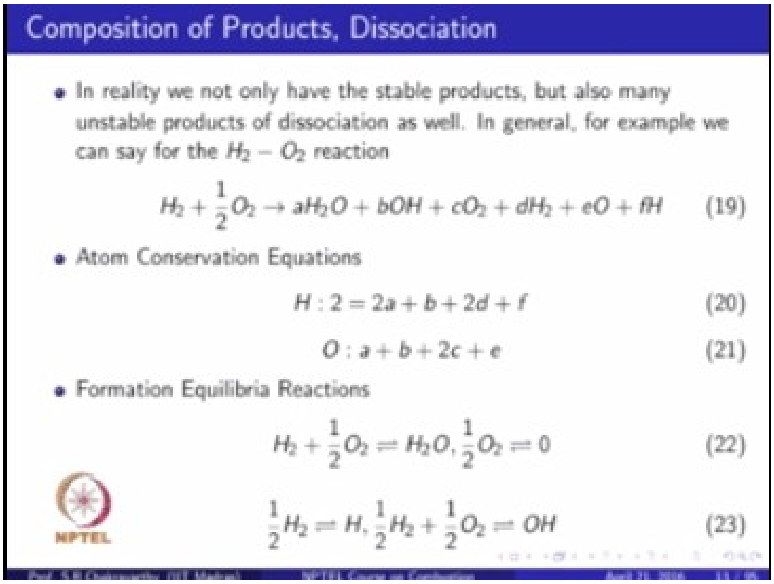
$$\frac{1}{2} O_2 \rightleftharpoons O$$

$$\frac{1}{2} H_2 \rightleftharpoons H$$

$$\frac{1}{2} O_2 + \frac{1}{2} H_2 \rightleftharpoons OH$$

So we now say H_2 +1/2O_2 gives and takes H_2O 1/2O_2 gives and takes O1/2H_2 gives and takes H and 1/2O_2 + 1/2H_2 gives and takes OH, so obviously when you write formation equilibria for H_2 and O_2 it is simply be H_2 gives and takes H_2.

(Refer Slide Time: 39:15)



Composition of Products, Dissociation

- In reality we not only have the stable products, but also many unstable products of dissociation as well. In general, for example we can say for the $H_2 - O_2$ reaction

$$H_2 + \frac{1}{2}O_2 \rightarrow aH_2O + bOH + cO_2 + dH_2 + eO + fH \qquad (19)$$

- Atom Conservation Equations

$$H : 2 = 2a + b + 2d + f \qquad (20)$$

$$O : a + b + 2c + e \qquad (21)$$

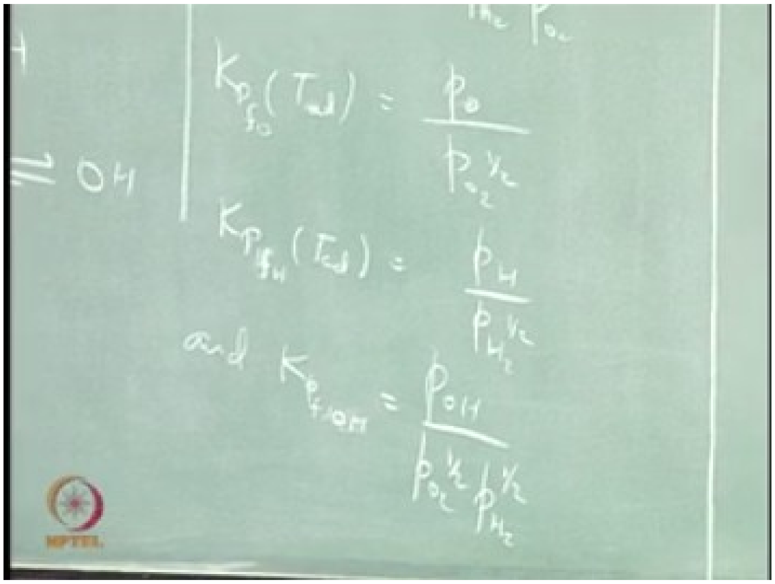
- Formation Equilibria Reactions

$$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O, \frac{1}{2}O_2 \rightleftharpoons 0 \qquad (22)$$

$$\frac{1}{2}H_2 \rightleftharpoons H, \frac{1}{2}H_2 + \frac{1}{2}O_2 \rightleftharpoons OH \qquad (23)$$

So there is this that is no news okay, you know there is that is no news and therefore there is no use okay, so here there is some use to actually considering hypothetical formation equilibria for non-reference element products okay, that is exactly what you are trying to do here. So with this one what can we write okay, we are assuming equilibria therefore we can write equilibrium reactions, equilibrium equations okay, so this means for these.

(Refer Slide Time: 39:44)

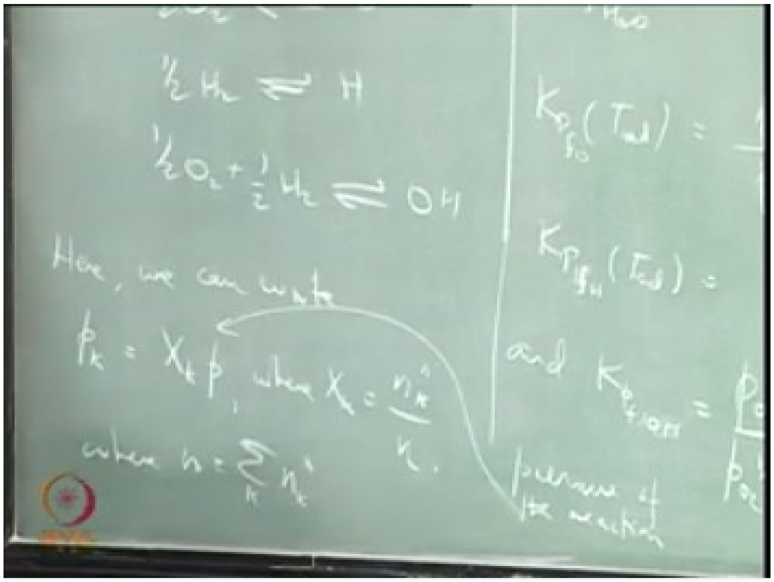


We can write K_{pf} at T adiabatic we do not know what is T adiabatic but we suppose that at this adiabatic flame temperature is where the equilibrium is existing between the hydrogen, oxygen and water high oxygen and the and its atomic form hydrogen atomic form and oxygen hydrogen and OH h right, so we have to write these at T adiabatic and then try to find out what it is, so $PH_2O/PH_2PO_2^{1/2}$ K_{pf} T adiabatic we have to have the subscript here for let us say O then is this $PO/ PO_2^{1/2}$ K_{fh} T adiabatic equals $PH/PH_2^{1/2}$ and Kph2 I am sorry OH equal to $POH/PO^{1/2}$ $PH^{1/2}$ right.

Now we did not bargain for the pressure to come in the partial pressure these are partial pressures right, we did not bargain for the partial pressures to come in there so we wanted to know we want to now change these partial pressures to the actual pressure total pressure, when I say total pressure it is not like the stagnation pressure and gas dynamics this is the total sum of all the partial pressures okay, this is the thermodynamic pressure okay. So now we are beginning to talk about the effective pressure you see the pressure at which this Eclipse this the entire reaction from the reactants on to the products is happening it is basically going to influence the proportion of the stable products versus the unstable ones okay.

So depending upon the pressure and depending upon the K_p equations the proportions of these are going to get altered okay, therefore the pressure is going to influence the existence and the amount of the unstable reactants that will soak up some heat and to the T adiabatic flame temperature of the products you see that is how the pressure is essentially coming into picture.

(Refer Slide Time: 42:47)



$\frac{1}{2}H_2 \rightleftharpoons H$

$\frac{1}{2}O_2 + \frac{1}{2}H_2 \rightleftharpoons OH$

Here, we can write

$p_k = X_k p$, where $X_k = \frac{n_k'}{n}$.

where $n = \sum_k n_k'$

pressure of the reaction

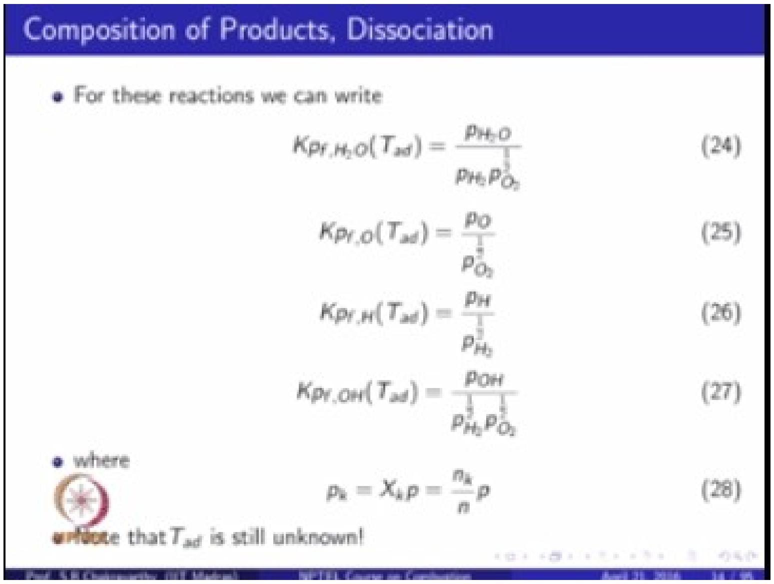
$K_{p_{f,O}}(T_{ad}) =$

$K_{p_{f,H}}(T_{ad}) =$

and $K_{p_{f,OH}} =$

So here we can write PK= XK times P.

(Refer Slide Time: 43:00)



Composition of Products, Dissociation

- For these reactions we can write

$$K_{pr,H_2O}(T_{ad}) = \frac{p_{H_2O}}{p_{H_2} p_{O_2}^{\frac{1}{2}}} \quad (24)$$

$$K_{pr,O}(T_{ad}) = \frac{p_O}{p_{O_2}^{\frac{1}{2}}} \quad (25)$$

$$K_{pr,H}(T_{ad}) = \frac{p_H}{p_{H_2}^{\frac{1}{2}}} \quad (26)$$

$$K_{pr,OH}(T_{ad}) = \frac{p_{OH}}{p_{H_2}^{\frac{1}{2}} p_{O_2}^{\frac{1}{2}}} \quad (27)$$

- where

$$p_k = X_k p = \frac{n_k}{n} p \quad (28)$$

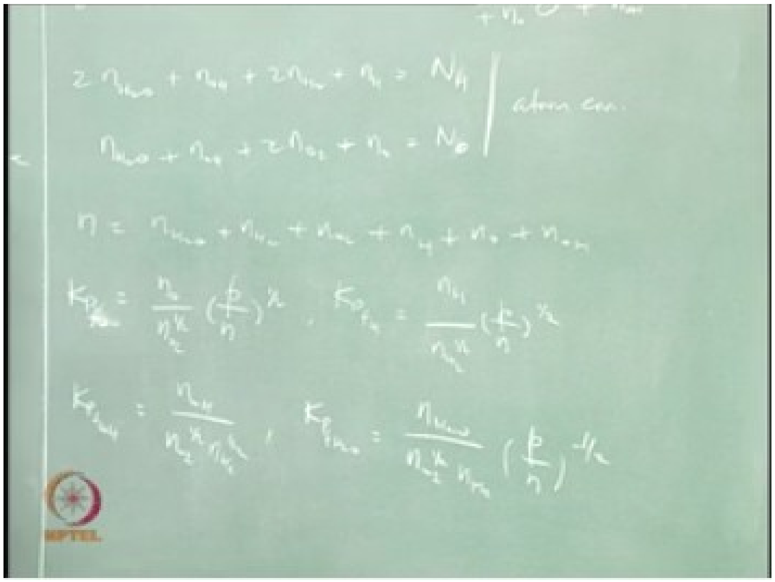
- Note that T_{ad} is still unknown!

Where XK equal to NK″/n where n=∑, ∑ overall K and K″ that means you add up all the number of moles of all the products together which we do not know yet okay, this is what you are trying to find out we are trying to find out the NK″ yeah, but whatever it is it is going to have total and the total will be n and then if you now take the value of n the Kth species ″divided by the total you will get it XK and XK times P.

So the P is the pressure at which the reaction is happening right, there is a pressure at which the reaction is happening then we are beginning to get the P in the picture and therefore you can now plug this inhere and all these things so effectively you are now going to get well in our case or for example if you now assigned numbers for K going from 1 to n let us suppose that 1 is the one corresponds to hydrogen, 2 corresponds to oxygen, 3 corresponds to water and so on then a would be n3″okay.

So in this thing we would now plug in n3″, n4″andso on okay, so effectively everything is going to be in terms of some NK″ all these things you can now rearrange them okay, so how do you do this.

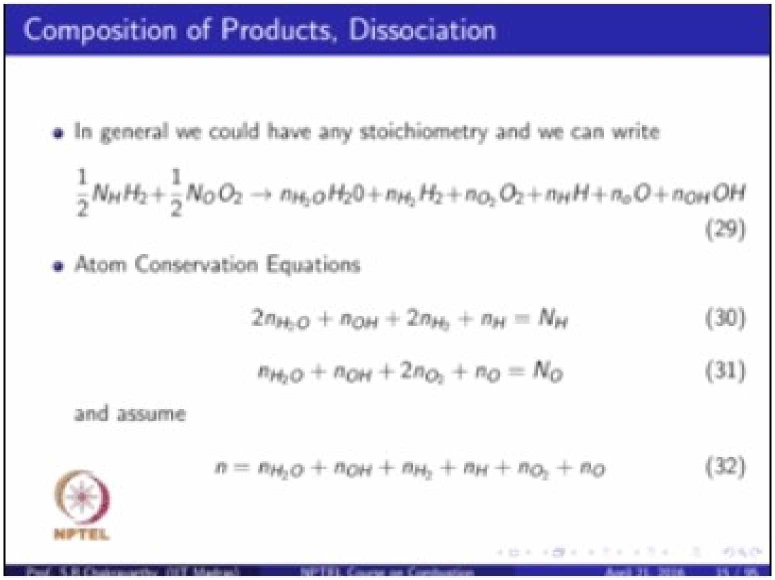
(Refer Slide Time: 44:57)



So in general we could have any stoichiometry right, given by let us say half an 1/2Nh H_2+1/2NO O_2 gives we now have to write NH_2O H_2O + N H 2 H 2 + No2 o2+Nh H+NO O+NOH OH okay, so am i just do not want to use ABC etcetera anymore because I might just cross 26 okay, there is that so many alphabet so many letters of the English alphabet so I will just keep N subscript whatever it is and then we get to NH_2O+ NOH +2NH2+NH=NO, NO essentially refers to the number of oxygen atoms in the entire system okay, we took a 1/2 NO because we have a oxygen molecule okay.

And NH_2O + NOH +$2NO_2$ + NO equals NH which is the I am sorry I made a mistake this is NH over there and NO over here these are the atom conservation equations okay, $N=NH^2O+NH^2+NO^2$+NH+NO+N2H okay.

(Refer Slide Time: 47:21)



Composition of Products, Dissociation

- In general we could have any stoichiometry and we can write

$$\frac{1}{2}N_H H_2 + \frac{1}{2}N_O O_2 \rightarrow n_{H_2O}H_20 + n_{H_2}H_2 + n_{O_2}O_2 + n_H H + n_o O + n_{OH}OH \quad (29)$$

- Atom Conservation Equations

$$2n_{H_2O} + n_{OH} + 2n_{H_2} + n_H = N_H \quad (30)$$

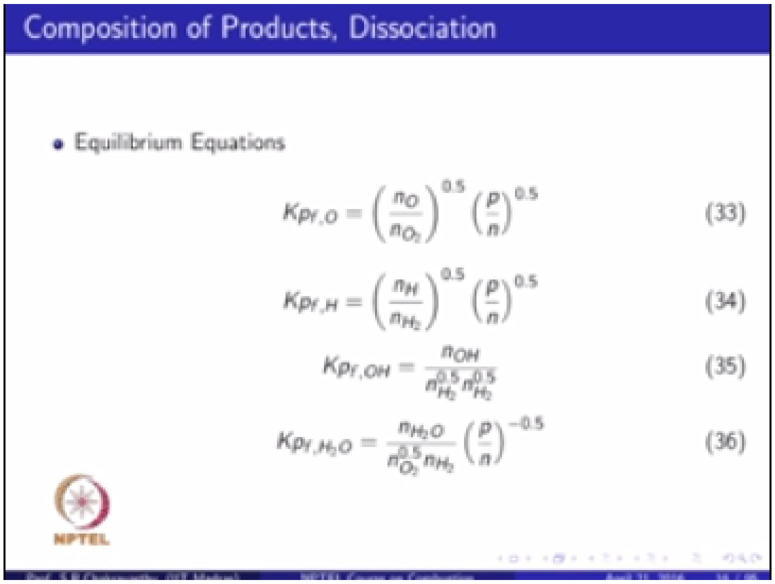
$$n_{H_2O} + n_{OH} + 2n_{O_2} + n_O = N_O \quad (31)$$

and assume

$$n = n_{H_2O} + n_{OH} + n_{H_2} + n_H + n_{O_2} + n_O \quad (32)$$

And KP, let us $KP1=NO/NO_2^{1/2}$ $P/N^{1/2}$ you now plug in these mole fraction information okay, in terms of pressure and N so strictly speaking we actually we can get rid of this and then say this is H_2O and no I am sorry, this is KPO or specifically we should say KP_{fo} this is KP_{fh}=NH/NH21/2 P/N1/2 and KP okay, KPFOH=NOH/NO21/2 NHO21/2 and the P gets cancelled here so we do not know it does not show up and then KPf H_2O equal to NH_2 O / $NO_2^{1/2}$ NH_2 and here pressure shows up with a negative exponent -1/2 all right from this we will now do this rewriting in the next class so effectively what we want to do is write each of these NO NH NOH and NH_2O in terms of NO_2 NH_2 because the denominators are all in terms of NO_2 and NH_2 okay.

(Refer Slide Time: 49:19)



Composition of Products, Dissociation

- Equilibrium Equations

$$Kp_{r,O} = \left(\frac{n_O}{n_{O_2}}\right)^{0.5} \left(\frac{p}{n}\right)^{0.5} \quad (33)$$

$$Kp_{r,H} = \left(\frac{n_H}{n_{H_2}}\right)^{0.5} \left(\frac{p}{n}\right)^{0.5} \quad (34)$$

$$Kp_{r,OH} = \frac{n_{OH}}{n_{H_2}^{0.5} n_{H_2}^{0.5}} \quad (35)$$

$$Kp_{r,H_2O} = \frac{n_{H_2O}}{n_{O_2}^{0.5} n_{H_2}} \left(\frac{p}{n}\right)^{-0.5} \quad (36)$$

And then we can plug that back in here and you will now get two equations and two unknowns okay NH_2 and NO_2 okay but those equations are going to look very ugly and then you have to solve that iteratively and then get the compositions once you get the composition you can go back and solve for the T adiabatic flame temperature using this equation okay, so continue from here tomorrow.

Production and Post Production

M V Ramchandran
G Ramesh
K R Mahendra Babu
Soju Francis
S Subash
R Selvam
S Pradeepa
Ram Kumar
Ram Ganesh

Udaya Sankar
Robort Joseph
Karthi

Studio Assistants
Krishnakumar
Linuselvan
Saranraj

NPTEL Web & Faculty
Assistance Team

Allen Jacob Dinesh
P Banu
K M Dinesh Babu
G Manikandansivam
G Prasanna Kumar
G Pradeep Valan
C Rekha
J Salomi
P Santosh Kumar Singh
Sridharan
P Saravana Kumar
S Shobana
R Soundhar Raja Pandian
K R Vijaya

Administrative Assistant
K S Janakrishman

Principal Project Officer

Usha Nagarajan

Video Producers
K R Ravindranath
Kannan Krishnamurthy

IIT MADRAS PRODUCTION

Funded by
Department of higher Education
Ministry of Human Resources Development
Government of India
www.nptel.iitm.ac.in