COMBUSTION

Lecture 5
Numerical Calculation of AFT, Chemical Kinetics 1

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So we are looking at this equation reaction where we are having a system of hydrogen and oxygen atoms where we have NH, NH number of atoms of hydrogen capital in O atoms of oxygen and they react and then we are considering six products okay. So we could consider a few more products and then the system is going to get a little bit more complicated correspondingly and the temperature is going to change, the final answer is going to change correspondingly.

So the accuracy to which you want the temperature depends on how much you want to go through the calculations and therefore you reside on the number of products you want to take right. So what we already saw is these are the active atom conservation equations right and then these are the hypothetical form a hypothetical formation equilibria, the equation or they are coming from there, so in the last class we wrote actually these expressions for this Kpf okay Kpfh etc. We have now rearranged in such a way that.

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Composition of Products, Dissociation

- The above equilibrium equations can be written in terms of the reference elements as

$$n_O = K_{pf,O} n_{O_2}^{0.5} \left(\frac{n}{p}\right)^{0.5} \tag{37}$$

$$n_H = K_{pf,H} n_{H_2}^{0.5} \left(\frac{n}{p}\right)^{0.5} \tag{38}$$

$$n_{OH} = K_{pf,OH} n_{H_2}^{0.5} n_{O_2}^{0.5} \tag{39}$$

$$n_{H_2O} = K_{pf,H_2O} n_{O_2}^{0.5} n_{H_2} \left(\frac{n}{p}\right)^{-0.5} \tag{40}$$

We will now get expressions for n_o n_H n_{oH} and n_{h2o} each of them in terms of n_{o2} and n_{H2} okay, so effectively we are now recasting everything that is there in the products in terms of only the reference elements okay. So the reference elements really are a key.
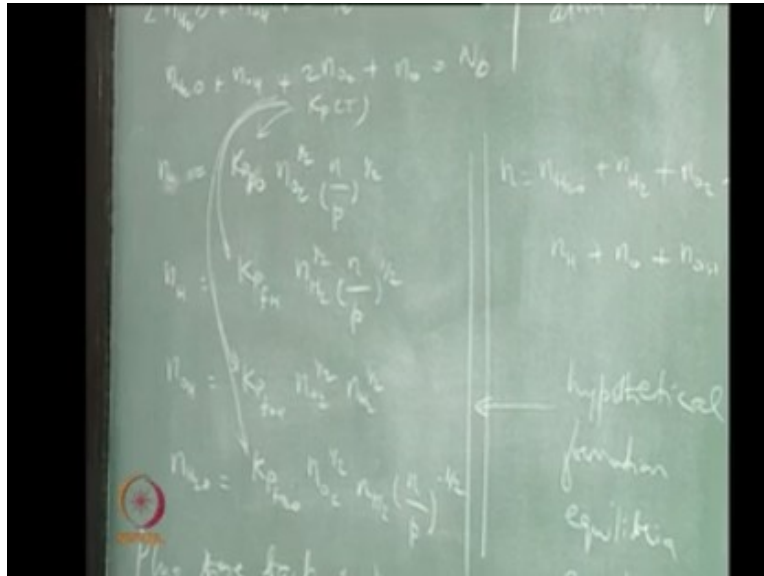
So once you do this you now plug these back in the atom conservation equations right and what are you going to get, so get 2Kpf H_{2o} n would be 1/2 and H2 to the n over P to the -1/2 that is 4 here + K_{Pfo} Hn what would be 1/2 and H2 to the 1/2 + KP f H that is for this, sorry yeah n_{h2} is already there I am going to write this towards the end, so K_P a K_{Pfh} n_{H2} to the 1/2 n over P to the 1/2 + 2nH2 = capital NH right running out of space there, so I'm going to write the next equation here it is not very different now.
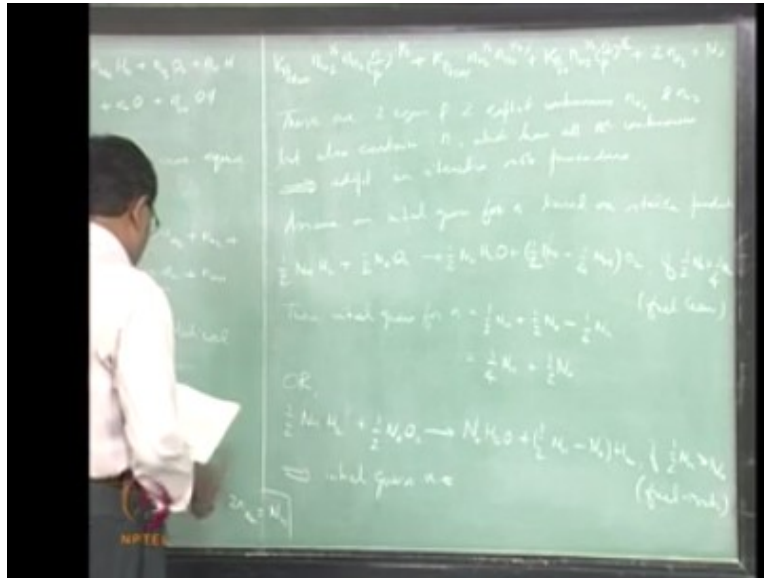
So or difficult now so Kpf H_{2o} n what will be 1/2 and h2 again or P to the - 1/2 + for the O_h we have Kpf H_{2o} h and we will do the half and H to the half we do not have an over P for this yes, + then we write for n_o and then we put the n_{o2} later on so we can now write this as Kpf H_{2o} oh it is here so n will do 1/2 n over P to the 1/2 + 2 + o 2 equals capital NO know right. So what we what we have now is we actually have two equations okay, two equations and explicitly speaking two unknowns.

The two unknowns being nh2 and no2 but implicitly we have an n sitting here now in a couple of places and that is a villain, it contains all the unknowns' right. So it is like you do not hear you have really not eliminated more unknowns than we want, therefore all the unknowns are there so you have to do this iteratively okay. So these are two equations and two explicit unknowns and h_2 and n_{o2} but also contains contain n which has all the unknowns, so which means we adopt a and E teal iterative solution procedure right.

So that is a bit of a combustion process if you are sitting in an exam you hope that you do not get a question on even one iteration to be manually calculated because, it is a little bit of a nightmare

so the first thing you have to do is do a initial guess for the end okay. So assume and initial guess for n based on stable products okay stable products, so we now have in n H h2+ 1/2 and no o2 gives half nh h2o+ half, I am sorry half in all - 1/4 and H times o2 if Auto is an excess right. So if how much excess we can actually quantify this if 1/2 in O > 1/4 and nH then initial guess for n = simply.

We are essentially looking at this + this okay so these are the final stable products to expect it means we disregard all the unstable products right and therefore we can expect this to be 1/2 n H + half nO - 1/4 in H and that would be 1/4 n sub H + 1/2 n sub oh yeah for this case, this is so this is like a fuel lean situation and or half an h+ often sorry, how half nH h2 + 1/2 + no2 gives an whoa amount of h2o this is actually doing an algebraic balancing okay. So it is sort of like interesting instead of a high school way of numerically balancing you do an algebraic balancing right.

So half NH - in all times nH2 where H2is now the excess species if half and H is then in oh this is the same assaying if 1/4 NH was greater than ½ you know KB about comparing hops and quarters there, so if you want to do the same thing you can do that this is fuel rich this implies initial guess in just add up these numbers so no + no + half and H - you know this simply want one 1/2 an nH right. So you can start with this initial guess for n and then have to proceed the other problem we see is these are actually functions of temperature here okay.

These and so on right and that is the temperature we are trying to find out okay, so we do not know what the temperature is but we need to take values for these, so that is like a big problem that is a huge loop okay. So what we have to do here is there are like about two or three loops that we have to think of we also are better off with actually so doing, this.
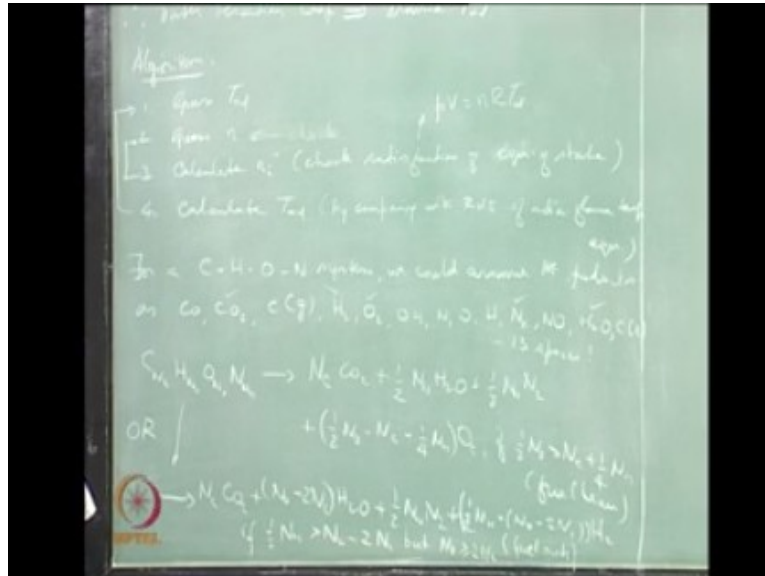
So we do not know the Kpf because the adiabatic is unknown these are all evaluated at T adiabatic in fact we should specifically say over here right, so therefore outer loop, outer iteration loop would be to start assuming assume okay, so you have to make an assumption you start with some guessed value for the Tadd and so then so the algo algorithm is now guess T and 2 guess n3 calculate and nidouble prime for calculate Tad okay by comparing with our RHS of adiabatic flame temperature equation because there is actually the enthalpy balance equation.

And then you go around right of course you can you can actually check, here check I am sorry between here and here you can check satisfaction of satisfaction of state equation or you can say equation of state right. So equation of state is essentially if you now have something like PV equals N or Tad so for the assumed T adiabatic okay if you know if you have now converged on ni double Prime okay then you should now get an N that is different from the guessed value okay and that final end that you get should satisfy this okay.

So there is something that we have not quite used up and therefore we can use this to check and then you go through this loop right. Now it is easier said than done because solving this set of

equations here it is actually pretty nightmare we are looking at a highly non linear equation so you are looking at products of unknowns and powers of unknowns that are non unity, so this is not very easy to solve. So this is this is pretty difficult to do to begin with and the more the number of products that you assume the more difficult the security equations are going to get.

The more the number of atom types okay you will now have more atom conservation equations and finally you will have in fact if you have more atom types you will have more products to consider, all right the first place so the hypothetical formation equilibria equations will flare up to as many products you have assumed and you have to now rewrite them and plug them back to as many atoms equations as you have the number of atom types. So all these things will become much bigger and so it is very difficult to do this.

So for example for a carbon hydrogen oxygen nitrogen system right we could assume the products, products as Co, c_{o2} carbon in gaseous form at these temperatures okay h2 o2 to oH no h n2 + oh2 o etc right and so then you have to so there are some initial guesses that we can also think about, so for C_{NC} H_{NH} Ono NH system right. So that means you have a system by which you have nc number of carbon atoms and h number of hydrogen atoms and so on so that means both the reactants are included like if you have oxygen there so oxygen could be figuring out in the hydrocarbon or oxygen separately or both okay everything put together.

So this could be like you know if you now consider one in its stable products among these look at how many products we have considered like, 1 2 3 45 6 7 8 9 10 11 12 already yeah did I miss anything to go to Hn oH into an Oh H – oh yeah of course I knew I was missing this we have a we have to consume carbon solid as well because that is actually the standard a reference element for carbon gas without that you are getting it stuck right. So that is about 13 species let me tell you that 13 species is actually not a very high number in reality okay.

So this is this is this is an easy problem okay so okay we are we looking at what could be a good initial guess right, so if you now assume that your stable products are let us say carbon dioxide water and let us say nitrogen and of course if it is a fuel lean situation you should get some oxygen out if it is a fuel rich situation you might want to get some hydrogen out, so I just put a

reverse stick to indicate that you will have one of these right, so if you know if you now do this algebraic balancing you can get something like h2o + half in n two + half in Oh - and C - 1fault in ho2 okay.

If half nO is greater than nC + 1/4 in H so it is kind of like this is the combination of the hydrocarbon for which you need to have so much oxygen in excess for a fuelled an combination to assume Oh - as a final stable product right. So this is a fuel lean situation for or okay let us start with this right there and then say this is good NC 0 2 + and nO H - 2 NCH h2o + 1/2 + n into that does not change and + 1/2 + H - n o -2 and c h2 right this is if 1/2 n His . n - 2 and C which is supposed to be but no is much greater than, so not greater than or = 2 and C right.

So we want to have this combination and then this should be less than the half and H this is the fuel rich situation, so if you do this then you can you can now get your initial guess for the end because all you have to do the fuel incase is to add in H+ often hey NC +1/2 NH + 1/2 NN + this thing and maybe may be cancel something in and unit. Now get the total in the initial guess okay the number of moles is not the same okay, so we are now basically looking at a initial guess for the total number of moles of the products based on these stable products.

Effectively what you are saying is we should expect these things that is sorry the NH no and OH etc to be in small quantities we expect largely the stable products but the other ones are going to be in small quantities higher the temperature more these will be okay and then they will try to bring down the temperature okay. So there is an equilibrium that gets attained by having more of these and getting the temperature down okay. So there is a reason why we are actually starting with an initial guess based on the stable products composition.

So if it is a feel rich situation you can add up these in order to get your initial guess for the total number of n, all right now the point is do we actually have to go through this Herculean task it is it is you try to do a computer code on this it would be a fairly good assignment for a course okay so and many times many students whatever not spending enough time on this do not succeed. So around the world that people can find aerobatic flame temperature realistically when it is going to be a Herculean task to write a code to do these things.

So the answer is there are codes available okay so most of the time we do not we do not have to sit and do these calculations all the time, we use some standard codes that are available so one of the most popular or standard computer codes or available.

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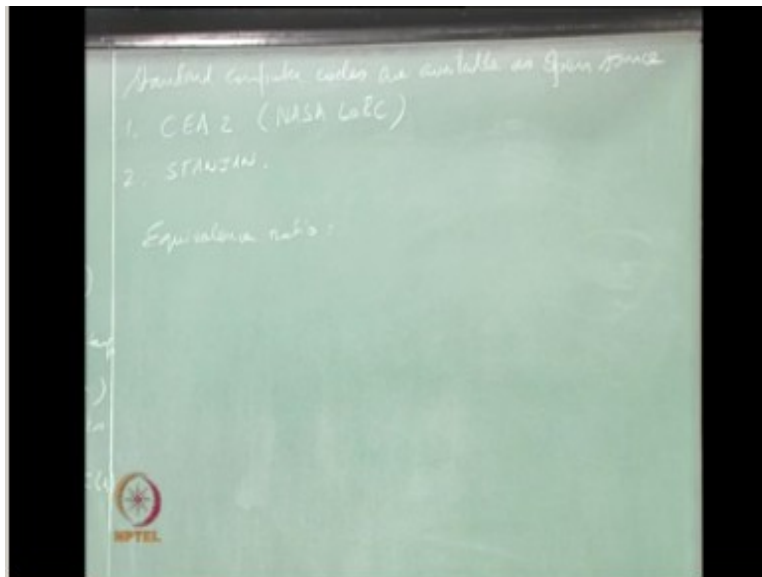
As open source okay well when I say open source typically bother only about getting the executable version do not worry about the source code itself, so the most popular one to the extent I know is the CEA2 - that is a current version of what is called the CEA that is that the CEA came out in 1996 the precursor to that was the CC71 which came up in 1971 and it was published in this DDC see 71 was published in this special publication called NASA SP 273, so many times people refer to NASA SP273 calculations.

Essentially they are talking about a latest derivative of this which is the CEA2 okay so it is actually available in the NASA Louis Research Center code. So you can look for these and download and so on we can I can I can give you more information about this there is also another one you can look at called STANJAN so on so there are actually many more codes enders available you can look up look up, but effectively in fact I want to point out one thing about

CEA- it not only gives you things like the Bribery flame temperature it also gives you other things.

Like for example transport properties of the product mixture so the protein all have a product mixture it can also calculate course typically you are expected to you know obtain molecular rate of the mixture, for example the ratio of specific heats for the mixture and but the but what more in this can do is to also get your thermal conductivity and viscosity those kinds of information also. So it is very extremely useful to have this code up and running for most applications that you want to view you get into doing some engine calculations or rocket calculations this is almost like the starting point okay.

You have to have this with you for you to be able to do anything more so what I will do later on is to put out some sample calculations in the website. So that we can go through numbers on let us say you now throw in some CP data like polynomial fits or something like that or make an assumption on calorically perfect gas and say constant CP but you need to look at typical numbers for these and so on so again we can do this and in fact I can also show you if you assume only the standard products let us say if you now take methane plus oxygen and give you a carbon dioxide and water we can we can go through the calculation and you will find that the temperature is actually shooting up beyond about3000 you know Kelvin.

But if you know add some more and then let us say you would from a CA to kind of thing you now have a huge list of species that you have assumed for the products you will find what the temperature is for the same composition of methane and air that you considered and so on well so we can we can put up put out those kinds of exercises in the website as we as we go along which we can look at but we have spent a little bit more time than intended on the aerobatic flame temperature calculation finally before I close this module I think I should mention something very, very basic.

Okay so one is this is the definition of what is called as equivalence ratio we did not quite get an opportunity totally about this because we first talked about what is called as a stoichiometric ratio but then we were devoted at the time by what is meant by heats of formation of the products

okay because the definition of the stoichiometric ratio involved that we have to actually get the most stable products which have the most negative heats of formation it standard heats of formation d then we were diverted into that and then that was right that is quite correct so to have that happen so we have to now get and get the job done right so we know talk to the industry people they keep talking about something called the equivalence ratio.

Okay so the equivalence ratio is typically given the symbol π and this is defined as the fuel, fuel air ratio for a given condition so this is given, given by fuel air ratio at stochiometric, stoichiometric proportions so in other words you do not really worry about exactly what the stoichiometric filler ratio is okay and of course you can also think about what if air is not the oxidizer okay and not, not all of air is oxidizer we need oxygen part of it is typically the oxidizer the nitrogen is likely like an inert it does not matter you can look at it fuel oxidizer ratio or fuel air ratio okay and you now forma equivalence ratio that is like this which means $\phi=1$ is stoichiometric, stoichiometric and $\phi<1$ is fuel, fuel lean and $\phi>1$ is fuel rich okay.

Now the rocket people like to operate fuel rich whereas the air-breathing engines people like to operate fuel lean okay so the rocket people do not really talk about a fuel-air ratio they talk about an oxidizer fuel ratio all right so when you talk about an oxidizer fuel ratio you could write this as oxidizer fuel stoichiometric divided by oxidizer fuel given so you now invert this because you have inverted your numerator and denominator so that this, this holds you always have this is something that I used to get confused to say as a student okay do I define it this way or do a different that way or which way it should be it how do I invert and all that stuff do not think about all those things what matters finally is this if you are $\phi<1$ its fuel lean you have to define your fight like that.

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Composition of Products, Dissociation

- Step 1 : Assume(guess) an initial adiabatic flame temperature (T_{ad}).
- Step 2 : Guess n
- Step 3 : Compute n_i''
- Step 4 : Compute T_{ad} using the computed n_i''
- Step 5 : Go back to step 1, until convergence
- Definition of Equivalence Ratio

$$\phi = \frac{(f/a)|_{given}}{(f/a)|_{stoich}} \qquad (45)$$

$$\phi < 1 \rightarrow \text{Fuel-Lean} \qquad (46)$$

$$\phi > 1 \rightarrow \text{Fuel-Rich} \qquad (47)$$

Okay that is how that is how it works and $\phi>1$ should be filled rich this is like the mantra all over the world on the on this okay so you don't have to think about this at all then you work out all of the details okay then I also want to emphasize these are mass ratios they are not the number of moles or molecular rate nothing okay nothing like that it is it actually the mass okay and many times in flow situations you could also use mass flow rates m dots so you can say m.m.f/m stoichiometric all right all those things are permissible but it is all mass ratios so with this I should stop this particular module and let me now get into the next topic which is chemical kinetics right.
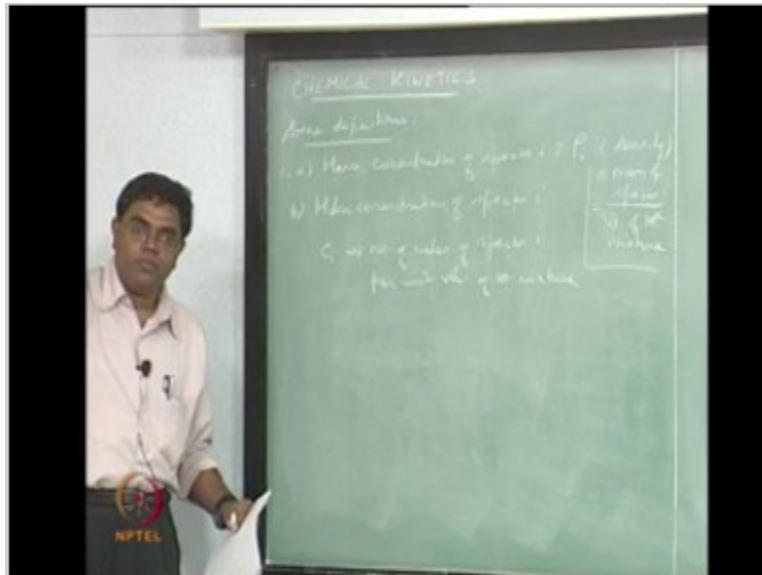
So let us now define some so keep in mind that we are still in the preliminaries okay we have not gotten to combustion yet okay so we have you have you have to learn I told you we needed to learn some thermal dynamics we needed to learn some, some chemical kinetics some amount of mass transfer leading up to flicks law and then we will get into some conservation equations derivation that is when we are actually getting into combustion at the moment not yet but we need these preliminaries so some definitions first some definitions first is one a mass concentration of species I okay what is mass concentration what is meant by mass concentration mass concentration what does it mean in what way we are looking at mass right.

So mass of that species in the total mixture in water the total mixture is it the mass of the total mixture sorry that is the next okay so you are looking at mass concentration so what, what would concentration really mean visit in volume so you want to say you now pick a unit volume of your species of your mixture okay and then you now look at what's the mass that is contained f a particular species in the mixture all right so what is this mass per unit volume density okay so this is something that we actually know right so this is this is basically this is given a symbol ρ_i which is the density okay this is equal to mass of species I in volume of the mixture right I am writing this in a congested manner because we are supposed to notice okay.

So you should not have to worry about this or maybe equal to sign here and then B because most of chemistry is done in moles okay so we also have now molar concentration of species I which is given a symbol CI C sub C sub I right now this is pretty easy game okay so what do we what do we know for CI or how do you how do you design define this not yet huh so this is basically number of moles number of moles of species I per unit volume so number of n_i per unit volume of the mixture okay.

Now I want to actually get the mixture density what do I do, do I take an average of all the all the species densities ρ_i can we think about this not yet yeah we want to know the mixture density so what is the mixture density okay you, you take a you take a unit volume of the mixture as we speak there is air around which is a mixture okay.

So will take a unit volume of the mixture and then find out what does its mass okay but we know that it is actually composed of many species and each of those species has a mass ρ_i pour in that volume because it we are now saying unit volume right so if you want to know the total mass of all the species in that unit volume I simply have to add all the masses of the individual species with a denominator being the same that is the volume okay so if I now split up the denominator for each of those I simply get back the sum of all the densities of individual species as the density of the mixture right.

So density of the mixture ρ right it is equal to $\sum_{i=1}^{n} \rho_i$ just have to add do not do any averaging or anything like that all right so just add all the densities to get the density of the mixture and similarly molar concentration of the mixture see is you just have to add the total number of moles there is there per unit volume right.

So total number of moles is like number of moles of the species plus number of moles of that species and soon in this volume therefore this is simply going to work out to $\sum_{i=1}^{n} C_i$ that is it and what is the relationship between CI and ρ_i one of one of them is number of moles okay per unit volume and the other one is mass by the per the same unit volume.

So the volume is pretty much the same for both so the only difference between them is on the one hand you are counting the number of moles the other one you are counting the moss so what is the difference between the number of moles and the moss what is the factor that the first sorry the molecular weight yeah so the molecular weight basically tells you what is the mass per one mole right.

Therefore if you have so many number of moles you need to have so much more mass as the molecular weight therefore the relationship is $CI = \varrho_i / w_i$ okay now these are things that are kind of confusing did you begin with if you are not used to as a reason why I am going through these things yeah rather slowly okay, so this where we now say W capital W I is the molecular weight of, of species I right the second definition that we want to have.

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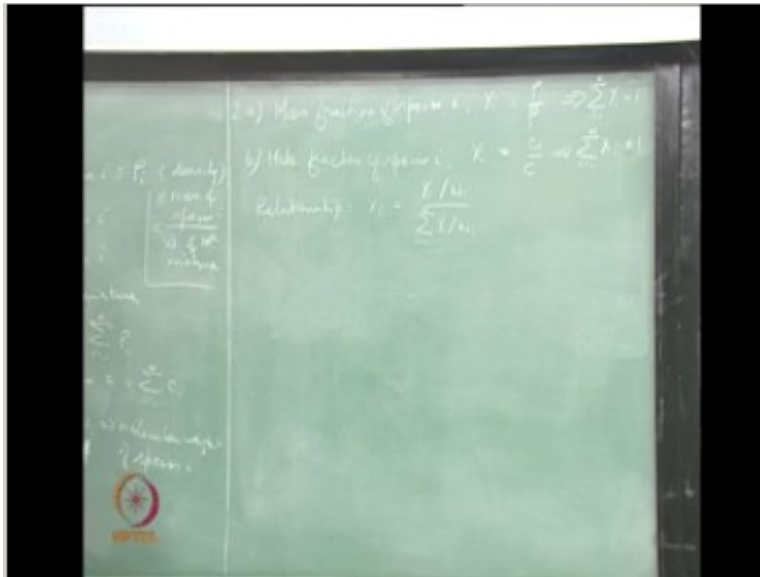
And I will try to use the next panel2a is mass fraction mass fraction and we use a symbol mass fraction of species I species I we use the symbol y I what do you think is mass fraction now this this is pretty indicative okay you can guess these things right so mass fraction is mass of species I divided by the total mass of the mixture right so of course you are not going to take like the mass of species I in the entire room and then divide by the total mass of the species all the

species in this entire room you could now basically think I will take a unit volume of the mixture look at how much mass I have of species I look at how much mass I have for the mixture in this unit volume so per unit volume basis which should work just as well okay.

Therefore we could we could say this is ρ_i/ρ all right now if you now are looking at the contribution of the species mass per unit volume to the total mass per unit volume of the mixture then if I add up all of these mass fractions what should I get one good so this implies that $\sum_{I=1}^{n} Y_I = 1$ and this is going to actually come in pretty handy to us later on because pretty soon here coming next week you will have lots of very dirty looking partial differential equations just read it and one of the one, one set of fun and then you will have sets of unknown so it's not just unknown so it is like sets of unknowns okay so we will now look a tone equation and say that is actually going from I equals one to n therefore there are n equations.

And there are three n unknowns and so on okay so this eat N and n is actually not, not too small okay so and we will talk about this okay so n could be of the order of flakes let us say 10 or 100okay let us about then let us say 10 200okay it will be very modest see really so you are now beginning to look at something somewhere between about 50equations 500 equations and all those things look like just write them ah so why, why I is going to be one set of unknowns right.

So in all these things Σ_{I} equals 1 to ny_i equal to 1 is going to now and how come, come to us like a big relief because it's a simple nice algebraic equation good old middle school days not even high school days okay so just deal with algebraic equation so it is great yeah so this is going to be one of the equations that we will actively consider among this dirty set of equations later on so similarly for B we can now say mole fraction of species I okay.

So the only thing that we are doing now is we know the trick what, what we want to do right so the only thing that we are doing now is to introduce the standard notation it is even as X I and as a matter of fact we introduced X as a most fraction last, last class right when we are looking at the how to do how to relate the partial pressures to the total pressure so X I XI is what he gets for this C I/C okay no, no big prices for this gash uh getting there so therefore, therefore here again

we can say $\sum_{I=1}^{N}$ capital X I=1 right one more and then what is the relationship, relationship is the ex I=Y i /wi / $\sum$ I=1 to n why i / wi alright.

So this is the relationship between x and y and this is also pretty important as we will see later on there are these mass transfer equations and chemistry chemical kinetics equations that are based on molar concentrations and mole fractions whereas when we try to do mass conservation we are more interested in mass concentration namely density and mass fractions all right soon the one hand for the fluid dynamic kind of equations conservation equations of mass momentum energy we will be dealing with moss or a mass basis whereas for the chemistry.

And so on we will be dealing with the mole basis molar basis and there this set of equations that is relating the mole fractions to the mass fractions is going to come in handy okay we need to have these set of equations in fact what will happen and I tell you this you have to recollect this and I can I again comeback to this we will have to treat both excise and Y eyes as unknowns okay so one set of equations that will link the two is this equation the set of equation this is actually valid for every species in the mixture right.

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Chemical Kinetics

- Mass Concentration of Species $i = \rho_i$
- Molar Concentration of Species $i = c_i$
- Density of the mixture $\rho = \sum_{i=1}^{N} \rho_i$
- Molar Concentration of the mixture $c = \sum_{i=1}^{N} c_i$
- Molecular Weight of Species $i = W_i$

$$c_i = \frac{\rho_i}{W_i} \tag{48}$$

- Mass Fraction of Species $i = Y_i = \frac{\rho_i}{\rho}$, $\sum_{i=1}^{N} Y_i = 1$
- Mole Fraction of Species $i = X_i = \frac{c_i}{c}$, $\sum_{i=1}^{N} X_i = 1$

$$X_i = \frac{Y_i/W_i}{\sum_{i=1}^{N} Y_i/W_i} \tag{49}$$

So we will have this relationship also come up in a big way alright so with these definitions we can now get into some kinetics and, and right now what I am going to do is to only bring in some notation okay.

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So we so we now talk about what is called the law of no of mass action right and the axiom that you are working with is atoms or atoms and molecules cannot react unless they collide okay there are exceptions to this okay there are exceptions like for example you can heat a molecule and then it starts vibrating and, and dissociating and so on.

So it does not really collide it any other molecule it can also be photo since photosensitive that means like light radiation or electromagnetic radiation can create these kinds of vibrations and stuff so there are exceptions but at the moment let us not worry about this and we have to start with this exam now strictly speaking we need to actually get into the details of this axiom as in how the collision happen.

And so on only when you are getting down to something like a kinetic Theory level okay or kinetic theory of gases level or even further if you want to get into something like quantum

statistical mechanics so if you have to now work out the collisions how they happen and what is the statistics of these collisions and how the energy exchange happens and all those things we would not do any of those things here thankfully right I just try to scare you there okay what we are going to do is to adopt a continuum approach so in a continuum approach what you essentially mean is at a particular point in the flow field you have a nicely defined density concentration mole fraction mass fraction all these things how you got that it is not your problem okay it is there again you can you can assume that it is there.

So with this we will actually be looking for laws that that are just taken for granted at the continuum level rather than derived from molecular level so the thing that we were basically looking at is let us start with an example, example is let us suppose that you now have h2 plus half o2 gives h2o here with this we can write a change in the number of moles of h2 okay and then we divide this by negative 1 to indicate that this change is in the manner of depleting this, this number and similarly we now write this as change in the number of moles of o2 / -half to indicate that you have a half amole that goes for every one mole of hydrogen and it goes therefore you have negative okay.

So this negative indicates depletion and the half of the one indicates the coefficient there and that is equal to one for every mole of hydrogen that is produced you have plus one mole of hydrogen water that is produced right so this is actually three equations yeah so you can now look at this is one equation this is another equation and these two together is another equation each of these three equations effectively relates what should be the change in the number of moles of hydrogen for a corresponding change in the number of moles of oxygen and so on okay and the signs effectively tell you whether they are getting depleted versus getting produced okay.

So if you can write this like this then in general in general we can write D n1 divided by double prime minus nu I single prime plus = DN 2 divided by sorry µ1µ 2 double prime minus µ2 single prime etc that is like you can write me and I knew I double prime minus nu I single prime where we had this notation or we can say Sigma I equals 1 to N nu I single prime M I gives Sigma I equals 1to N mu I double prime M I.

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So this is like a generalization of what we just went through and let's now call this leeks I work sigh is what's called the degree of advancement of the reaction let me stop here for the day.

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

K R Ravindranath

Kannan Krishnamurthy

IIT MADRAS PRODUCTION

Funded by

Department of higher Education

Ministry of Human Resources Development

Government of India