Indian Institute of Technology Madras

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National Programme on Technology Enhanced Learning

COMBUSTION

Lecture 16
Conservation Equations for Multi-Component Mixtures

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We have been looking at flicks law with the hope that we should be able to relate the diffusion mass flux to the concentration gradient so that we would now reckon the concentration gradient let us say in terms of a mass fraction as one of the primary unknowns then we should start thinking about what would what would be its corresponding equation okay so when you now want to solve the combustion problem that means you have to actually find out how the composition of your mixture of reacting species changes yeah so you, your reactant the species concentration is a is an unknown and therefore correspondingly you need to have an equation that determines it and the equation that we will be looking for is the equation of conservation of mass of species.

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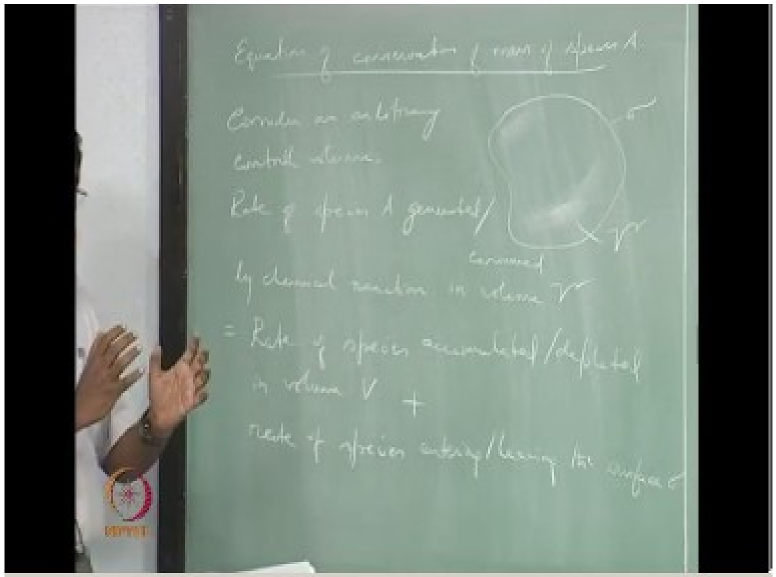

This is a general mass conservation equation for a particular species as an extension of what we have already seen before in the in the case of the thermal thermo chemical processes that we have looked at like constant volume constant pressure fixed mass reactors and the well stirred reactor and so on so there we had a very limited approach to conservation of species mass but here we will try to actually have the most general approach that is possible that would include convective effects as well as in the most general way as well as diffusion effects right so we want to now bring those into account in addition to unsteady effects that there are possible.

And chemical reactions right so the way you want to do this is to now consider a arbitrary volume so can now look at this as like a hey volume so shedding best place to give a 3d effect there the surface as the surface is denoted by σ and the volume itself is denoted by script v and so we consider I consider a an arbitrary control volume I like to emphasize that the arbitrary arbitrariness of the control volume is pretty important for us okay and that is what actually tries to make it quite general for us and we will probably try to get the same equations in the end but we will invoke the arbitrariness of the control volume to do this pretty soon.

So then the question is how do you how do you conserve moss the answer is just like you consider anything else okay so how do you conserve anything the answer is so you now look at a situation like let us say a control volume and then you have to now keep an account the rate of rate of change of whatever you want inside the control volume as equal to whatever is coming from outside versus what is going out what is coming in okay so this is pretty general as I have said earlier you know this you need to do this from looking at your bank account on how much money you have like versus how much money is getting depleted versus what is coming in and what is going up.

And so on so this is a very intuitive idea nothing great greatly mathematical about it so what we will first do is write the conservation equation like a sentence okay like a like a verbal statement so that it just appeals to us appeals to a common sense without getting into mathematical notation so here rate of species a generated/ consumed by D by chemical reaction in volume V in volume V is equal to rate of species accumulated or depleted in volume v plus rate of species entering or leaving right entering or leaving the surface σ okay so there are three things that are happening primarily one you have species getting generated or consumed within this control volume okay and you have species coming in and going out of the control surface so if you now look at how much of your species a so we will be looking at a particular species a okay.

So whenever we say see species we should be looking at species a here right the amount of species a mass in this case cable which the amount we are looking specifically at mass of species a that is accumulating or depleting the rate at which it is accumulating or depleting how much of it is growing or decreasing it depends on how much of it is generated or consumed within the control volume okay plus how much if it is entering or leaving on the control surface so in other words will now see that there are these three things right generated or consumed accumulated or depleted entering or leaving and you have all these things with a it is a slash in between to say this or that.

And you can always look at whatever is from the left hand side of the slash they should kind of go together that is if something is generated okay or entering it will get accumulated if something is getting consumed there is it disappears or it leaves it will get depleted okay they all go together so this is fairly straightforward for us okay the second thing that I would like to point out in this verbal equation is two of them or happening in the volume the other thing is happening across the surface okay so keep this in mind we will have to apply the Gauss's divergence theorem to convert the surface term to volume term that is what that is why I am basically looking at this okay.

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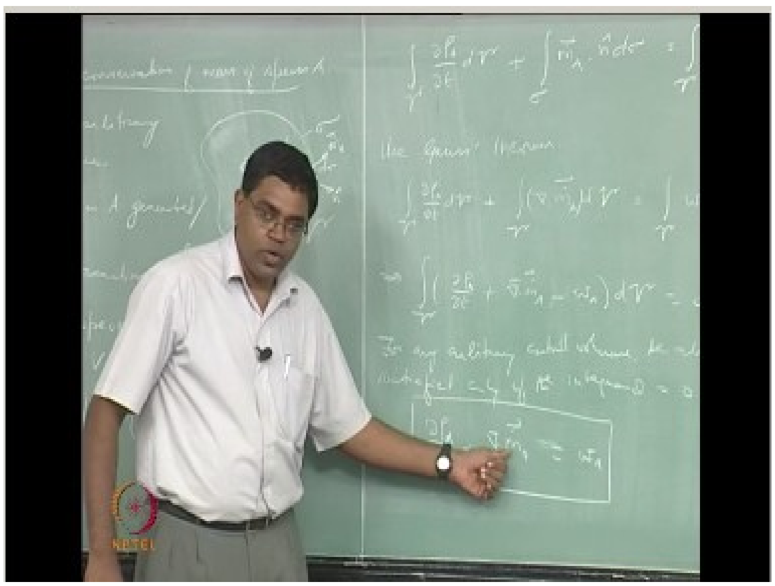

So this can be now written as then a integral over the volume dough row a who would do t DV+m dot s vector dot n hat d sigma equal to integral over the volume w a DV all right here this is the first term on the right hand side of the verbal statement which is to say the rate of accumulation or depletion so how did you get this ϱ DV is the mass in an elemental volume that's inside this control volume.

So you now have a DV that you want to integrate over the entire volume ultimately so ϱ times ϱ a times DV so ϱ is the density there are 0 as is the density of species a times the elemental volume is the elemental mass there and do by T of that is the rate of rate of mass accumulation a depletion right we all want to worry about the DV being changing in time because that is like fixed in time.

So the only thing that is accumulated that is changing is the density itself right there is a sense that is like the mass concentration as I said so the concentration of the species is changing in time and so this is the rate of accumulation or depletion term that is a volume term we can see that it is a volume integral the rate of mass entering or leaving the control surface is the second term on the right hand side of the verbal statement which we now put on the left hand side of the second term here.

So this m dot m dot a m dot a is the mass flux okay so we have looked at this as a mass flux so essentially what happens is if you know where to look at a little window on the surface as a d σ this has a m dot m dot a vector mass flux that is cutting across at an angle to let us say that is your n hat if this is your unit normal locally all right to this to this elemental area D σ which we want to.

Now integrate over to get the entire σ this is the mass flux that we are looking at that is going at an angle so if you want to now look at the projected mass flux it is coming out there should be the dot product there right and this now takes care that the dot product will actually take care of and you now integrate over the entire surface whether it is going to leave or enter it will take care of that okay so the dot product could be negative or positive depending upon whether it is going to be entering or leaving okay.

So here was we know is the is a reaction this is the mass reaction rate this is not the molar reaction rate k we are looking at the amount of mass that is produced per unit volume per unit time so this is actually going to be the units is going to be per meter cubed second right so this is not this is not to be given by the law of mass law of mass action.

And Arrhenius law you need to you need to use that expression and multiply by the molecular weight of the species a in order to get this because this is Mark's all right keep that in mind all right now so we now notice that two of them or volume terms this is a surface term therefore we now use the Gauss's divergence theorem to convert your surface term to a volume term as well and so we now have a volume term for the first as before plus a volume term for the second as well now which is the divergence of m dot a vector DV equal to integral signal over volume w a DV so what you can do is a group of them row a dodo you over do t plus divergence m dot a I am sorry -W a DV =0 here is where we now invoke the arbitrariness of the shape the control volume that we have considered okay.

Now if this integral has to be 0 over this integral for the entire volume for any arbitrary volume in general that is possible only if the integer and is 0 right so we now get from here for any arbitrary control volume the above can be satisfied the above integrally should specifically say double integral equation can be satisfied only if the integrand equal to 0 so that implies 0aoverdue t plus divergence m dot a vector is equal all right.

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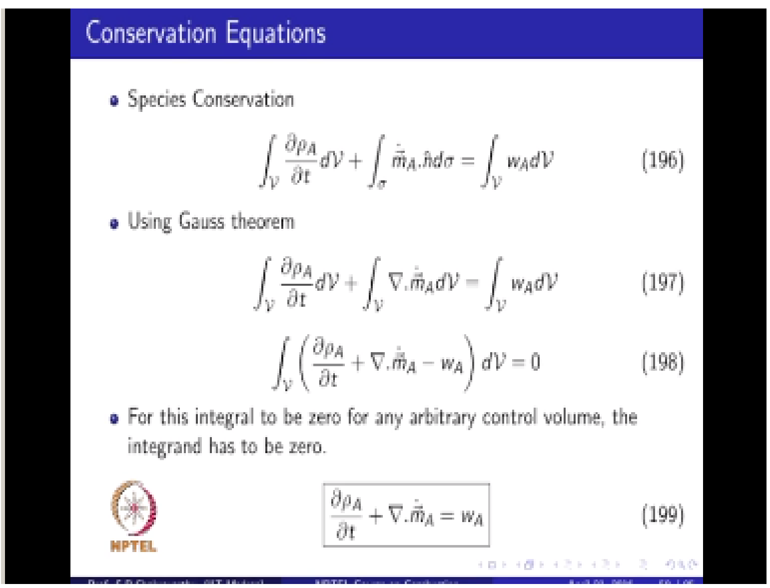

We are still not quite looking at the three fundamental processes of combustion showing up here although we see three terms okay this is a unsteady term but this actually embeds convection and diffusion together because we now notice that this is actually corresponding to a row a VA vector V vector is the velocity of species a in a laboratory fixed coordinate system or a stationary frame of reference okay and then we will now have to split it into the mixture average the mass average velocity of the mixture and its diffusion velocity when you do that then we will get into a conductive term and a diffusion term separately in addition to the reaction term that is showing up already okay.

Then we will begin to see the three basic processes convection reaction diffusion reaction okay so that is where we are heading you can now do this for species B okay so let us let us say we now say similarly speech is B do we have to do this again shall we right so how do I how do I do this or I am just going to do is wherever I see am just going to replace a by B that that is that simple so I can write guru be we would do t plus divergence m dot B vector is equal to W be now let us just go back and call this equation one in this class and let us call this equation 2 okay let us now try to use flicks law okay using fixed lock using flicks law for a binary mixture of species a and B okay as a reason why we wrote another equation for B is it is not like we want to have fun with all the letters in the English alphabet.

And so on right so if you now have a fixed law then how do you how do how does this work out we can we can now say guru a over duty plus divergence row a V vector equal to divergence row be gradient why a plus be over t plus divergence rv equal to divergence row be good heed YB plus I am sorry w be alright is there a problem I guess not we had a m dot m dot B let is put let' is pick door be in this panel and m dot B is a row BVB vector okay so vector could be now written as V vector plus capital VB vector okay so you know right split that and then you now get your row be V vector this is the mass average velocity of the mixture of A and B then you have the other part you have the Robbie capital d b vector and that is actually vector for we had a negative row be gradient why be alright.

And you now try to take it on the right hand side you now have a row be variant YB we already had a divergence so we now have the same thing outside alright so this is how we have actually got these two equations now what happens when you try to add the set so here okay before we do that so we can now begin to see that this is the unsteady term okay this because the process could be unsteady we now have a rate of depletion or consumption of as please you know generation of or accumulation of a in an unsteady process so this is an unsteady term okay so I can now say this is unsteady term right this is a convection term right heat transfer people might probably use convection for natural convection okay but aerospace people are used to forced convection most of the time so maybe and then they might call this advection okay.

So we are like we are convective people so we connect so all the time therefore this is we just call this convection and this is the diffusion term right if you want to now generalize most conservation equations well you would call you have an unsteady term all right let us say for example looking at a momentum conservation you may have an unsteady momentum term you have a unsteady momentum convection sort of Europe you may have a momentum convection term.

This would be diffusion that would be a viscous effect okay and then this is this is the reaction term in our case but in general just this diffusion term could be referred to as a transport term okay or and the reaction term could be referred to as a source term in the case of momentum for example a body force could be like a source but in this case the chemical reaction a provides the source.

So these are these are typically what is going on so primarily what is happening is we have a convection diffusion or reaction that is coming up that is that constitutes your combustion process there is something that we have seen them in the past all right now let us try to do some interesting thing here let us try to add up these two equations right add the above what would you get you have a partial derivative of row a with respect to time plus partial derivative of ϱB with respect to time that okay now are looking at a mixture which has only two species right so ϱ a $+\varrho B$ is nothing but σ= 1 to 2 of σ I what is that is just a mixture density $\varrho a+ \varrho b = \varrho$ so effectively you now get a of by duty right so you now get do ϱ by DT plus you can do all the summation of our stuff through divergence.

And so on no problem so divergence of ϱ a times V vector plus divergence of ϱ B times V vector is nothing but divergence of $\varrho+\varrho B$ times V vector so a plus ruby is again row so this is divergence of ϱ times vector right so this is divergence of ϱ V vector equal to let us look at what happens here right divergence of Road EAB well if you if you are very picky we should probably put de DBA here right p we just want to do like computer we wanted wherever you got an a here we put a Band vice versa to construct this equation right so we should have put DBA let us do that but then we noticed that b is equal to DBA we saw that the other day right and so did these two are the same row is the same in both and then you have a gradient.

So all that is going to happen diversions of road EAB times gradient of why a plus YB what is why a plus YB as one okay now have a mixture and why a and YB or mixed of fractions okay and this mixture has only a and B so the tooth the two factions together should become unity right and what is gradient of 10 okay so you now get a 0 what does that mean is it because gradient of 1 = 0 that we get this edition right it actually tells us the same thing as what we saw the other day for be equal to DBA if species a is mixing into species B then species B is mixing into species they are just having fun with each other nothing else is happening outside.

This so you do not have a extra to the notice that this is act this and this are actually coming out from surface terms right so it is as if like these two together or all happening inside there is no extra mass of the mixture as a whole that is entering or leaving because of the diffusion process if you now put things together right so that is exactly why the diffusion flux is the diffusion mass fluxes of all the species together will equal to 0.

It all looks like they are all interacting with each other but the some effect the net effect of this is nothing there is really no net mass exchange by diffusion of all the species put together in a mixture okay, this is a very important idea that comes out of what we are doing here.

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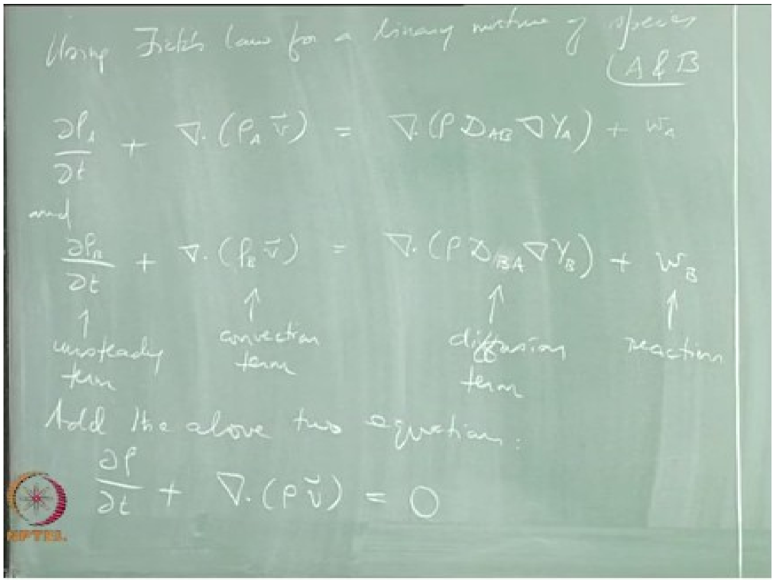

plus what do you get for WA + WB can we just write that there if it were a n component mixture right where we had subscripts like I for the IH species equation we would have written like Σ i = 1 to n Wi would be should we can be we did it in the past we have the Σi = 1 to n the question is did we have a WI or did we have an ωi and does that matter Greek or English did that matter did not matter if you were to be looking at ω or i that is a number of moles of species I produced per unit volume per unit time okay.

And you try to sum over all the species you might find that there is like a net mole production in this reaction that we are looking at okay but here you are looking at W which is the mass that is produced per unit volume per unit time right, so if you now try to add up the mass that is producer consumed keep in mind things have to get consumed if things have to be produced right if mouth of species I produced per unit time producer consumed per unit time per unit volume + Mars of species be produced to consume per unit time per unit volume right.

What would that be that should be = 0 because if you cannot have a depleted or consumed you cannot have reproduced or vice versa as far as mass goes because mass is conserved in a chemical reaction because chemical reactions or only based on electronics changes and nothing to do with nuclei right, so you get a zero again okay so does not look good to have any question with two zeroes right next to each other sufficient right one and what do we have do we recognize this yeah.

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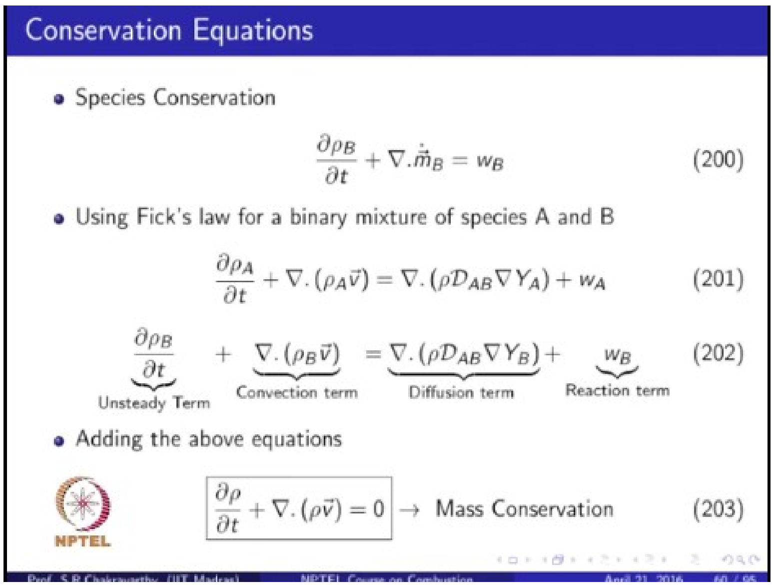

So this is basically your continued equation of the mixture as if there was no diffusion going on no reactions going on so when your aerodynamics professor writes this equation for flow past and air foil okay F air flow passed an airfoil right.

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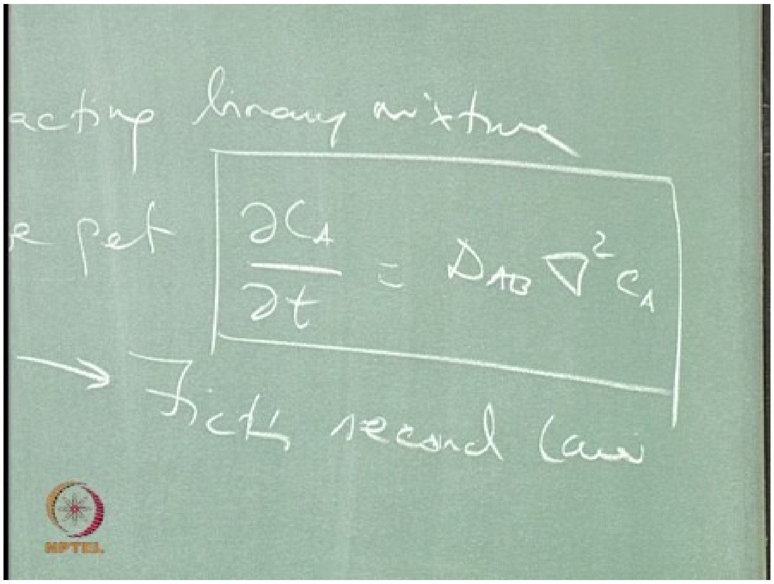

You could strictly speaking argue with them him or her that there could be chemical reactions and diffusion of spices going on and you would not know would you write that is what that is as that is as far as the mixture is canceled okay the mixture does not really feel these things as far as the mass of the mixture mass conservation of the mixture you will find that there are effects in the energy the mixture and so on okay.

But as far as the mass the mixture is concerned you did not matter that you had a multi-component reacting, so is not that kind of interesting right, so you get back your mass conservation of a mixture as if it is a non reacting single component situation okay now for fun let us also have one more thing that we can do we could we could write we could write conservation a species conservation equation we will simply call the species conservation equation.

The stuff that we have done here will simply call this a species conservation equation okay so we could write a species conservation equation on a molar basis okay will pretty much get the same thing except that we will just change our notation we will not use ρ we will you see we will not use EM we will use n we will not use w we will use ω right so simple right so we could write $\partial C_A / \partial t + \nabla . n_A$. vector = ω_A alright.

Can you do what I said before what will happen if you now write the same thing for species V and you look at only a binary mixture okay what do you think will happen you will get $C_A + C_B = C$ right and you can you can also get a similar expression we were here we would we want to get nice is because we never really do a mass conservation kind of thing for mole conservation for a mixture or a non reacting single component species flow right.

But then what is going to happen is this two terms are corresponding to terms for this we will have X_A and X_C we will have X_B and right you now add these two you will still have zero because you are not going to get like ∇(XA) + XB which is 1 again right just like YN YB right so this is going to be 0 but $\omega_A + \omega_B$ is not going to be 0 right that is the only difference okay now you can do a couple of you can do one more thing we will have a I am sorry we will have a V* will have a CV*r okay.

We keep that in mind so using Fick's law we get $\partial C_A / \partial t$ + ∇CAV * which is the molar averaged mixed a velocity = ∇ of CD_{AB} ∇ XA + ωA right now for a for a quiescent non reacting binary mixture what is meant by questioned effectively we say v * = 0 right and what is non reactive what is meant by non reacting ωA =0 right each of those ωA ωB will be 0 right so we get $\partial C_A / \partial t = D_{AB} \nabla$ CA I am ∇^2 that is CA right. This is what is called as Flick's second law I remember studying this in high school in a verbal as a verbal statement.

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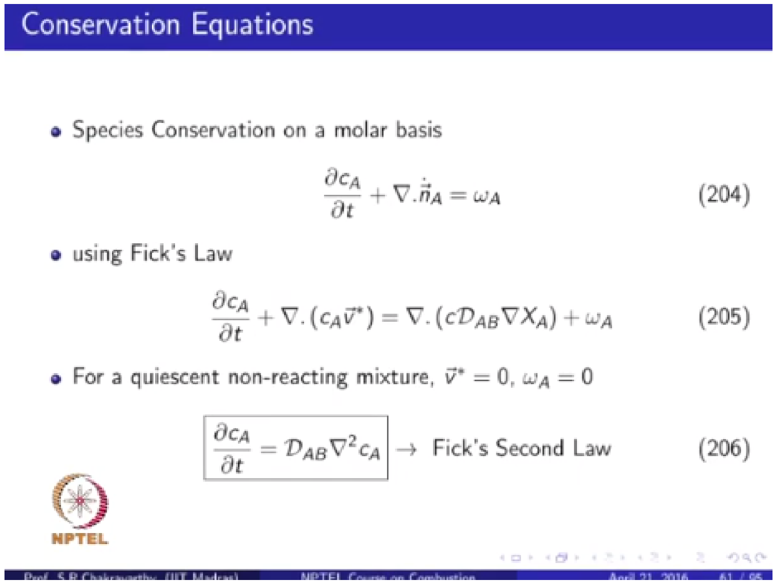

Along with the flicks first law of course but later on I found that students in subsequent years have not how to fake it all okay now what is the second law say it says something like if the first law were to mean that the diffusion mass flux is directly proportional to the concentration gradient okay the second law then says that the rate of change if the concentration is directly proportional to the second derivative of concentration okay.

So the mass flux is proportional to the first derivative the rate of change of concentration is proportional to the second derivative this is how the fixed laws were formulated but we can find that the first law that we started using cannot be derived from continuum point of view it is stated as a law okay we said we needed that law because we wanted a connection between the mass flux the diffusion mass flux that is what else the species is doing other than going with the rest of the mixture.

We needed a expression for that in terms of a primary variable namely the concentration so that was a constitutive relationship that the ficks first law provided to us and it can be obtained only if you get down to molecular level you need to get into at least kinetic theory or quantum statistical mechanics those kinds of approaches in order to be able to derive it from principles right.

So you now go through a like a course like a physical gas dynamics in order to explain how you can get ficks law okay and went and the two not necessarily very satisfactory alright so that is a that is a fundamental law whereas the second law is something that you can actually find out from molar conservation work for a specific for a special situation of non reacting quiet some binary mixture right.

So this is not as special as the first one good now where were we started talking about mixing there is diffusion we have been stuck with binary mixture binary mixture is boring can we need something more right so let us look at what to do for a multi-component system now it is truly multi-component system.

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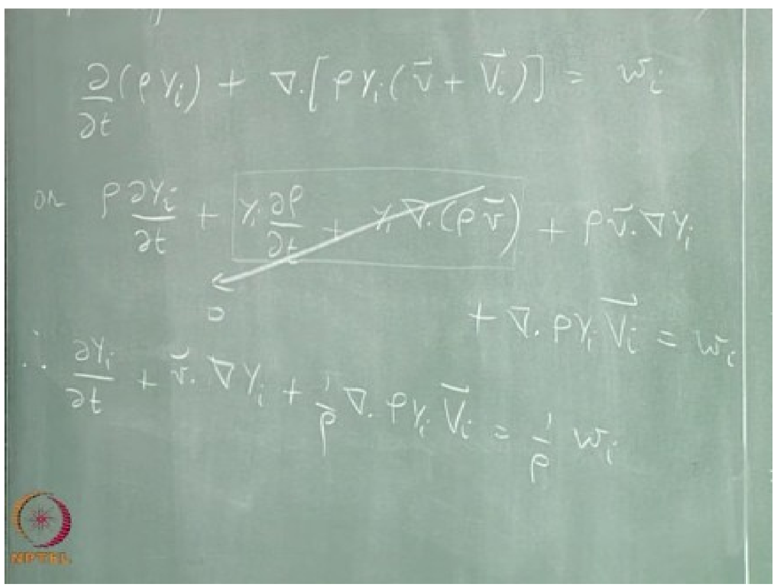

In a truly multi-component system when you say truly that means it is not even binary that is what it means binary is multi component okay but by is not multi enough okay, so we want to have a like at these three so he the how these are the simplest situation a three species becomes complicated okay for us so a in a truly multi-component system that is more than two species.

Right then we can write the species conservation equation okay on a mass basis of course that is to say an equivalent of this particularly something intermediate between this and this that means we will now be we will now say let us open up m. A as ρA times V + ρA capital V_A we will do that but then we will start blinking because we do not know how to write ρA capital VA which isJA in terms of the concentration gradient because Fick has not said this for us for more than a binary mixture right.

But we can go up to that point so we will write this equation by just opening up into a mixed or average velocity and a and the diffusion velocity we will write up to that point and then we will start blinking okay so not yet at the moment okay so he can go ahead so we then say and unless otherwise stated it is always going to be mass basis from now on we will never really go back to molar basis.

Okay so we will now write this as a ρ Yi this is writing for the iH species right so ρ A can be written as ρYa all right so similarly I am going to write ρ Yi over here for the Yi iH species + divergence again I am going to write ρA as ρYA or ρ Yi times I am going to write this is V mass average to mixed a velocity V + Vi right = Wi or can now try to do a few things pull out the ρ use chain rule.

So you can write Yi ∂ρ/ ∂t + Yi divergence ρV with a mixture average velocity + ρV. ∇ Yi + divergence ∇ yi times Vi = Wi okay so the way we is written up is to group these two together right and then notice that this is just Yi times this so therefore this can go out all right and therefore you have a ∂ Yi / ∂ t + V. ∂ Yi + 1/ ρ divergence ρ Yi Vi = 1/ ρ Wi.

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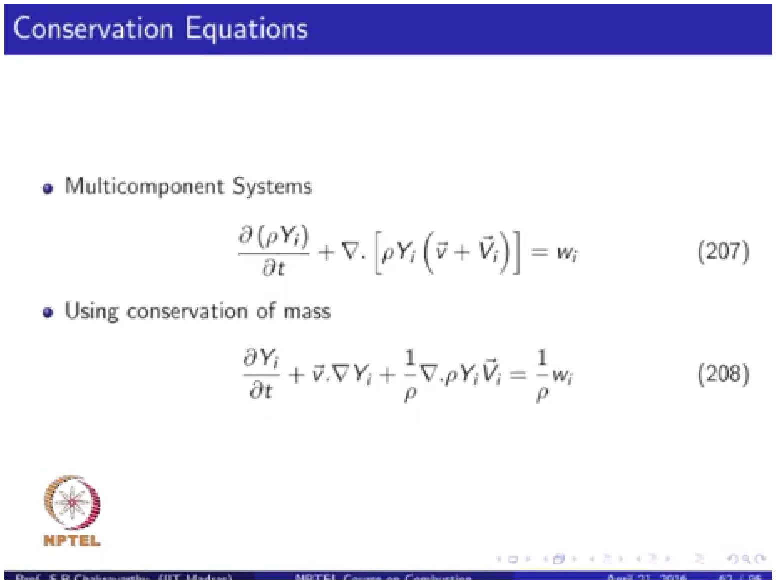

This is built this is good enough to begin with because we can we can get some insights into what is going on you can see that this together case a ∂ / ∂t + V. ∂ of Yi right what is ∂ / ∂ t + V. ∂ that is the material derivative D/ Dt of Yi.

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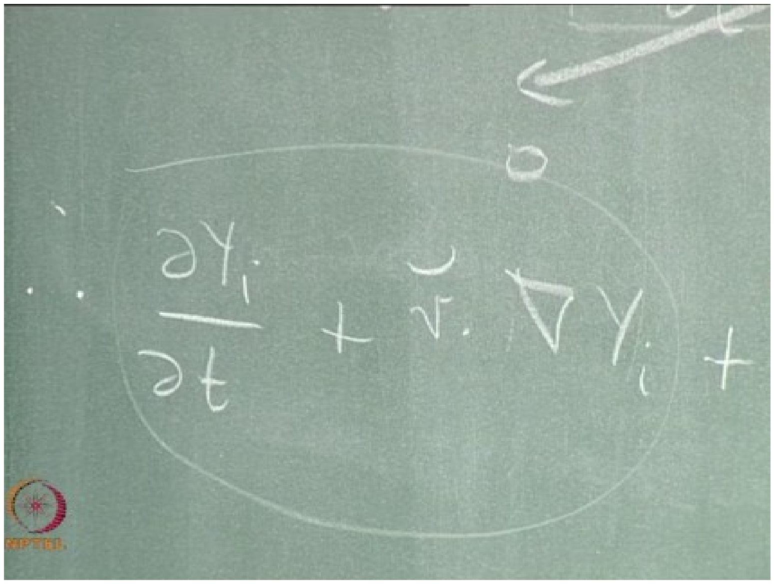

Okay so in Lagrangian frame of reference you would simply look at a rate of time rate of change of species mass fraction Yi as far as this is concerned all right, so this is actually together then called inertial term okay.

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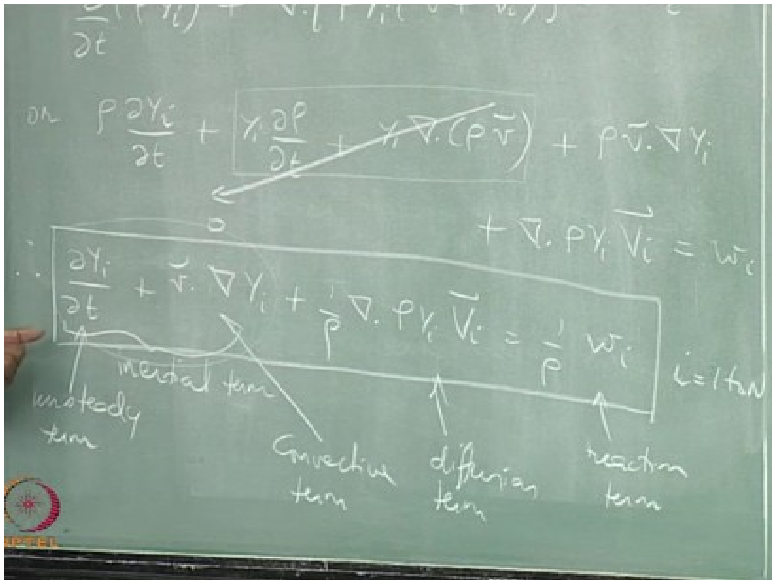

This together is called the inertial term inertial term of course you can in an Illyrian frame of reference we notice that there is a basic change in the concentration because of time with respect to time as well as there is an apparent change because of its motion all right so this is this is this is the distinction between an Illyrian and Lagrangian frame of reference if you were to go with the particle you will not know that you are moving therefore you will see everything as only a rate of change of time.

That is what indicates your material derivative right but then you now step back and say her a minute how the changes that I went through is because I was truly changing + I was also going go experiencing the world around me as I was moving this is happening in our lives right, so this is a lot of philosophy in fluid mechanics you see you see stop thinking about this it is very intuitive okay.

So if you now look at an Illyrian frame of reference you can now identify this as the unsteady term like before and this is you are truly a convective term right now the moment you see your capital Vi that is your diffusion mass diffusion velocity okay that is the relative velocity of species I with respect to the mixture right so this is your diffusion term and as before this is your reaction term right.

So you always have to learn to read equations term by term and try to assign meanings those terms physically then a mathematical equations begin to look like sentences in English okay or your favorite language right and these are basically words okay it so happens that these words are composed of Spelling's that are very jumbled looking for from a language point of view but that is what that is.

The equation tries to tell you something and it is a string of words that make sense and you have to start looking at each of those terms like words that make sense right and of course you know you are to keep in mind x + and – x there like the verbs and all the all the things that that other there are thrown in between these meaningful words to convey the meaning for the sentence as a whole right.

So this is what we are essentially looking at for the species conservation equation we still have a problem we do not know what is capital Vi vector all right but you had a heap in mind now that you are looking at looking at a truly multi-component system this is one equation that represents actually n equations and n could be pretty large okay it could be 5, 10, 40, 100 not more than that mostly A so this is a equation that is actually consisting of large number of equations keep that in mind okay.

Then the next problem that we have is we have to start looking at a much more generalized version of ficks law for actually multi-component system that tries to relate your V to Yi Vi to Yi and you might be worried Vi is a vector Vi is a vector so it has three components okay so we are actually having three n equations that we should be looking for but fortunately if you are now going to be looking for Vi in terms of gradient why I all the 3 components or buried into just one unknown Yi.

Weather system out of taking gradients in different directions for you to get your Vi right we hope that we will now be able to get a fixed law to work for a multi-component system but unfortunately it is not going to be as simple it is going to take some more time for us to get there we will start doing what is called as the multi-component diffusion equation tomorrow.

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