Chemical Engineering Principle of CVD Processes
Prof. R. Nagaranjan
Department of Chemical Engineering
Indian Institute of technology Madras
Module-2
Lecture 19
CVD Transport Phenomena: Effect of Homogeneous Reactions on MTAC

Welcome to the next lecture in our course on chemical engineering principles of CVD process. In the last class we define something called the mass transfer analogy condition in which the mechanism of mass transfer and heat transfer are identical therefore you can essentially take an appropriate non-dimensional distribution in, that you have obtained by energy conservation.

And from that extract the corresponding mass fraction distribution for example that you will get when you do mass conservation and the ability to apply the mass transfer analogy condition greatly simplified or analysis of the problem and also reduces the requirement for experimental data collection but as we also saw there are certain conditions in which the mass transfer analogy can be violated and in such cases you cannot do that.

I mean you pretty much have to do you experimental measurements separately, you have to do measurements for velocity distribution, measurements for temperature distribution and measurements for mass fraction distribution and similarly when you do your analysis, modelling and simulation you have to write the conservation equation and constitutive relationships for mass conservation, energy conservation, momentum conservation separately and solve them completely.

So there are certain conditions which introduce an additional force for mass transfer but which do not violate the mass transfer analogy condition, one example we looked at was the Stefan flux which is induced by mass diffusion flux towards the surface but it is not considered an analogy breaking condition because the effect of Stefan flow is identical on heat transfer and on mass transfer.

So we can still continue to use all the approximations that we normally use when we have mass transfer analogy conditions. In fact the place where you have to pay particular attention to the Stefan flow is when we talk about quiescent conditions within the boundary layer we have been assuming in all of our flux calculations that there is a laminar sublayer around the substrate in which diffusion dominates and in which convection is absent.

Now typically as you know the condition for the importance of convection is sent by the Reynolds number, if the Reynolds number is much less than 1 which all that quiescent flow. However when we talk about quiescent flow conditions corresponding to mass transfer it is not sufficient to write it only in terms of Reynolds number.

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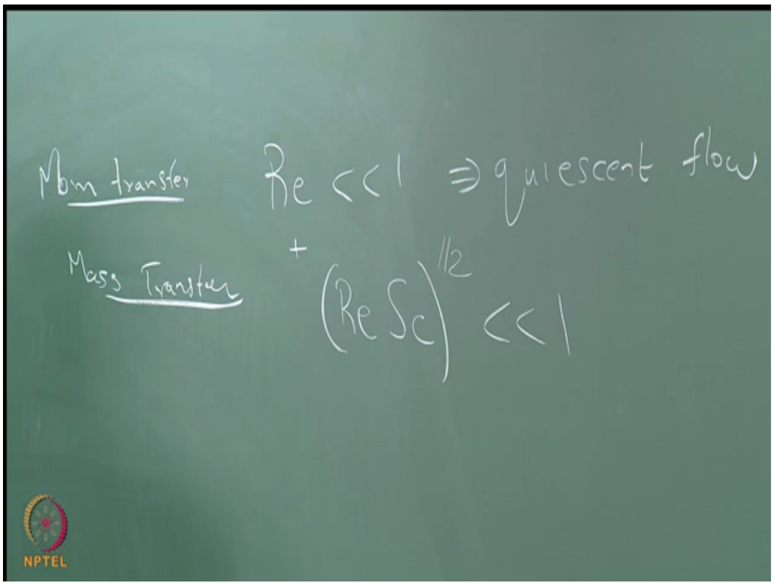

Mom transfer $Re << 1 \Rightarrow$ quiescent flow

Mass Transfer $+ \, (Re\,Sc)^{1/2} << 1$

So in terms of simple momentum transfer you could say that Reynolds number much less than 1 implies quiescent flow but again this is on the basis of momentum transfer. However if you want to establish quiescent conditions for mass transfer there is an additional condition that applies which says Reynolds number times Schmidt number to the power half must be much less than 1.

Another way to think about it is even if you have a flow that is quiescent in nature if the mass transfer conditions are such that the Schmidt number is very high then it is possible that you could violate the quiescent's criteria. So you have to really take the multiple of roles number times Schmidt number, the square root of that has to be much less than 1.

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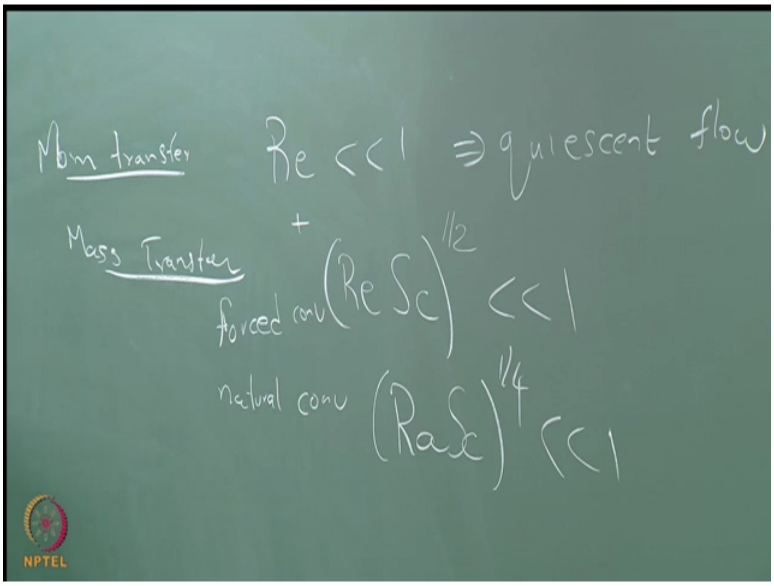

Mtm transfer $Re << 1 \Rightarrow$ quiescent flow

+

Mass Transfer

forced conv $(Re\,Sc)^{1/2} << 1$

natural conv $(Ra\,Sc)^{1/4} << 1$

Now this is the case where force convection dominates in the case where natural convection is dominant, the corresponding criterion is in terms of the Rayleigh number that we defined in the last class times Schmidt number and in this case it is to the power 1 by 4. Rayleigh number times Schmidt number to the power 1 by 4 has to be much smaller than 1 for us to assume quiescent's with respect to mass transfer and in fact there is even an additional condition that Rayleigh number.

By the way this is the Rayleigh number for mass transfer, that is the condition is Rayleigh number for heat transfer times Prandtl number to the power 1 4 must be much smaller than 1. The reason for this is, that when you have natural convective heat flow that can again induce mass flow. So finally in the case of natural convection you really have to satisfy both this condition as well as this condition and this condition.

3 conditions are need to be satisfied when you are talking about ensuring quiescent with respect to mass transfer in a natural convective flow situation whereas in the case of forced convective flow where there are 2 criteria which is the Reynolds number must be much smaller than 1 and Reynolds number times Schmidt number to the power half should be less than 1.

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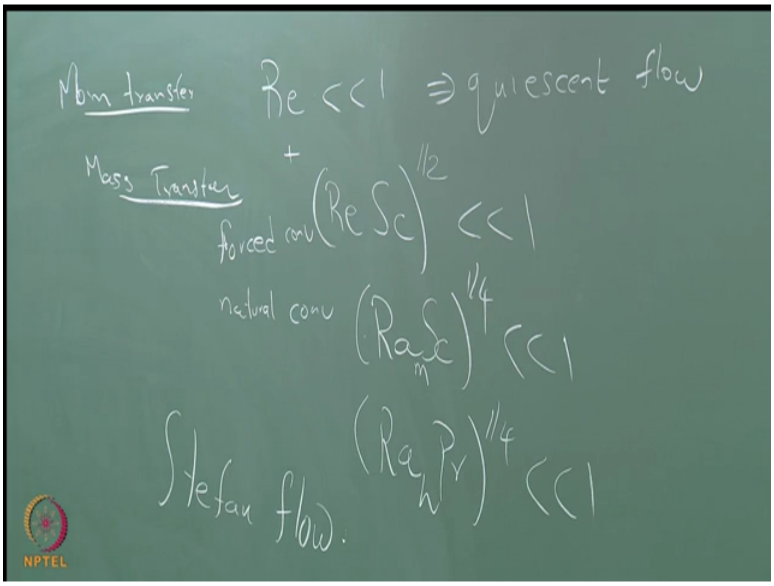

Now where does the Stefan flow enter into this? Stefan flow essentially induces an additional convective flux which must be taken into account when we do this calculation. So under condition where Stefan flow is important the Reynolds number will have an additional component to it. In addition to the mainstream convective velocity U or induced natural convective velocity there will also be the velocity that is associated with Stefan flow.

So now you have to define an effective Reynolds number which includes the contribution from Stefan flow as well. So you could again have situations where all the conditions for quiescents are satisfied. However the diffusive flow of a nondilute species induces a sufficiently large opposing flow that it actually contributes to the convection in the system sufficiently that the condition for quiescent is violated.

So in other words when you have a CVD process in which the depositing species is not a dilute species that can itself induce a convective flow which can violate your assumption of diffusion domination in the diffusion sublayer. So the Stefan flow effect even though it does not really influence the mass transfer analogy condition it can influence your very fundamental definition of a quiescent layer around the substrate.

So it needs to be taken into account in determining whether a quiescent situation really obtains or not. If the condition for quiescent is violated then what you have to do is, really apply a correction factor to your calculation to include convective transfer across the boundary layer in addition to diffusive transfer.

The other thing that you should also give in mind is that when we talk about the boundary layer adjacent to the substrate we have so far been assuming in most of our formulations of equations and it is a steady-state. However the CVD process can take a long time to reach steady-state sometimes it may never reach it.

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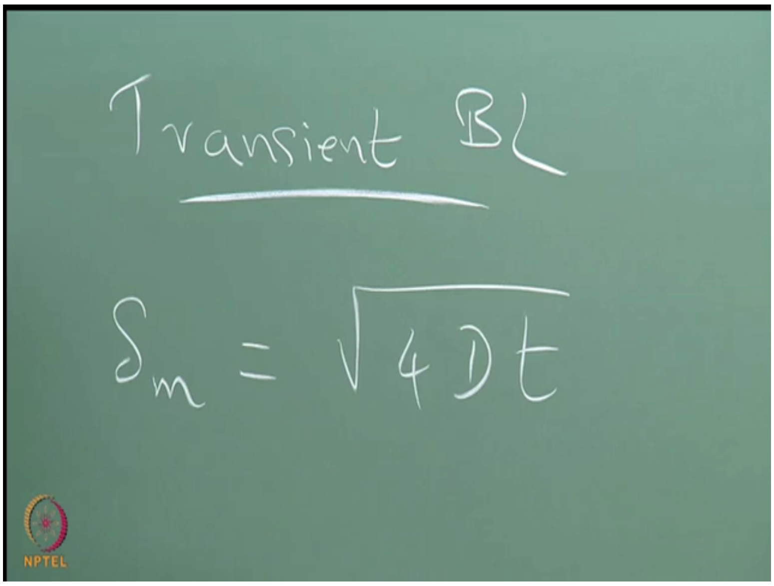

Transient BL

$$\delta_m = \sqrt{4Dt}$$

And so there may be a time dependence of the boundary layer thickness and that is usually when we talk about transient boundary layer the mass transfer boundary layer as a dependence that looks like this square root of 4Dt where D is the Fick diffusivity and t is time.

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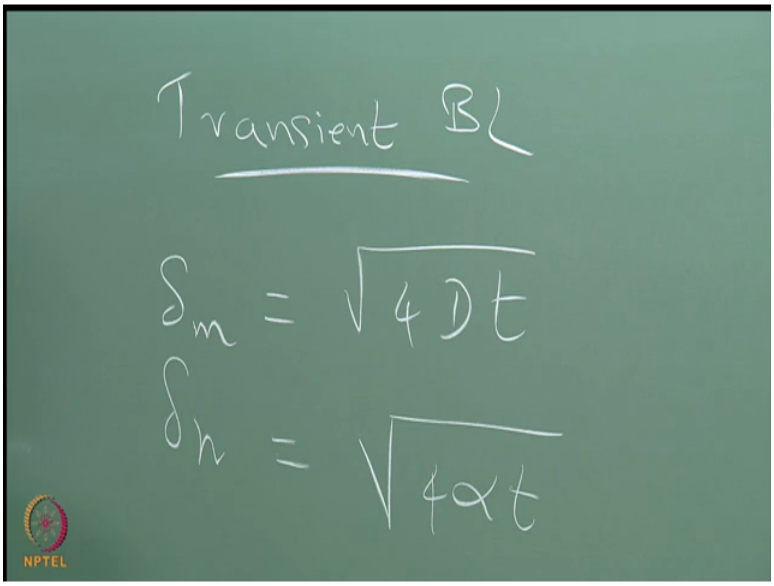

Transient BL

$$\delta_m = \sqrt{4Dt}$$

$$\delta_h = \sqrt{4\alpha t}$$

So basically has square root of time dependence and similarly the heat transfer boundary layer Delta h will have a square root of 4 times Alpha t dependence.

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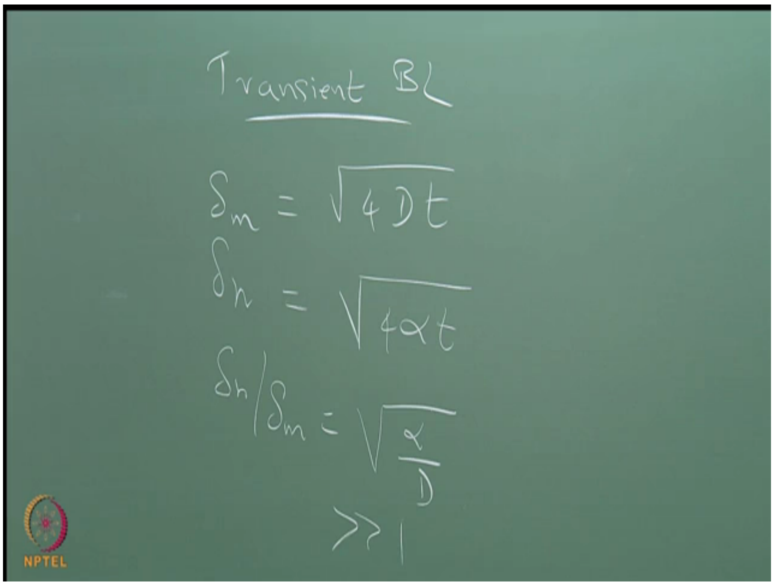

Transient BL

$$\delta_m = \sqrt{4Dt}$$

$$\delta_h = \sqrt{4\alpha t}$$

$$\delta_h / \delta_m = \sqrt{\frac{\alpha}{D}}$$

$$\gg 1$$

So if you look at the ratio between Delta h and Deltam it goes as square root of Alpha over D. Now in most physical situations thermal diffusivity which is K by Rho CP tends to be much larger than mass diffusivity. So this number is typically larger than 1 and most of the time it is much larger than 1. So the physical implication for that is, that the heat transfer for boundary layer is much thicker than the mass transfer boundary layer.

Which again, you know what that implies for us from a CVD viewpoint is that the affect of gradients in the temperature profile due to the existence of the boundary layer will set in well ahead of the affect of the boundary layer on the mass fraction profiles. So when you are doing your transfer calculations you have to make sure that you use the appropriate thickness in doing your calculations.

So first when you calculate your temperature distribution you have to use the appropriate boundary layer thickness and then from that value onwards you have to assume that the temperature profile follows a typical boundary layer profile and of course that is going to then determine the mass transfer distribution and therefore the mass transfer rates associated with it.

In a CVD system just like we try to avoid turbulence effects. We also tried to avoid transient effects, we would like to drive the process towards a steady-state as soon as possible because you know you want to run a very stable process where you can control your film thickness to plus or minus 1 percent of the nominal value.

In order to be able to do that you cannot afford to have a time-dependent boundary layer thickness because the boundary layer thickness is a determines the rate at which the depositing materials are transported to the substrate. So in a sense square root dependence on time could essentially imply a square root dependence of the film thickness on time as well and that again is not good.

So the way to avoid transient in a CVD system typically what is done is, you do not even introduce the substrate on which you are trying to deposit the film until you are sure that steady-state conditions have been reached. So you first start up your system to your temperature measurements and watch for a stable temperature distribution that is usually good sign that initial transients have been passed and now you are in the steady or quasi-steady-state.

You can also, if you have the ability monitor the last 3 distribution, the pressure distribution and provided all these measurements are showing a stable trend you can reasonably assume that your mass transfer also is going to reach steady-state around that point. So after you have verified the temperatures and velocities and pressure have stabilised then you introduce a substrate and watch again for the evolution, the time evolution of deposit thickness and hopefully you will see steady-state.

However some of these parameter values indicate that it will take longer to achieve steady-state with respect to mass transfer than it does to achieve steady-state with respect to heat transfer and momentum transfer. So you have to be prepared for some surprises, you know just because your temperatures and velocities have stabilised does not automatically mean that your mass transfer rates have stabilised as well.

And it also does not mean that you just wait longer and the stabilisation will happen because that may not be the case either, the lack of stability is something that can persist over a very long period of time it all depends on how you have designed your process how we have set up your process what are the interdependencies? You know as we have seen from our discussions mass transfer does not exist in isolation.

Even though that is the process that we have focused on we have to realize that depends very much on the momentum and energy or heat transfer processes that are taking place in the system and it also depends on the entropy in the system. Are we at a stage where we are driving towards the equilibrium or are we far away from the equilibrium? So mass transfer is a very complex phenomenon in a CVD system which, you know, as I said has to be solved for iteratively taking into account all the coupling between the mass transfer phenomena and the heat momentum and an entropy transfer phenomena.

Okay, so let us get back to our discussion of analogy breaking mechanisms that can happen. I mentioned in the last class that there are primarily 2 we should be worried about, one is Phoresis which is an applied force which acts on the species that are diffusing and depositing and it is usually represented in terms of Phoretic velocity C and we said that you can essentially establish a Peclet number which depends on the velocity, Phoretic velocity and you can then determine a correction factor for the Nusselt number which will depend on this Peclet factor.

And we illustrated that for the case of gravitational Phoresis, thermophoresis and so on. Today we are going to look at another mechanism that results in breaking of the mass transfer analogy and that is homogeneous chemical reactions that are taking place inside the boundary layer around the substrate. The reason that, again that breaks the analogy is because the affect of this homogeneous chemical reactions on the mass fraction profile in the boundary layer will be very very different from their effect on the temperature profile within the boundary layer.

And so you have to establish a correction factor for the homogeneous chemical reactions take into account the fact that the mass fraction profiles in the boundary layer or not what you would have predicted if there were no chemical reactions taking place in the gas phase. The condition where we suppress all homogeneous chemical reactions in the gas phase is called a chemically frozen state and that is typically what is assumed when people are doing modelling and simulation of CVD reactors because it simplifies the analysis quite a bit.

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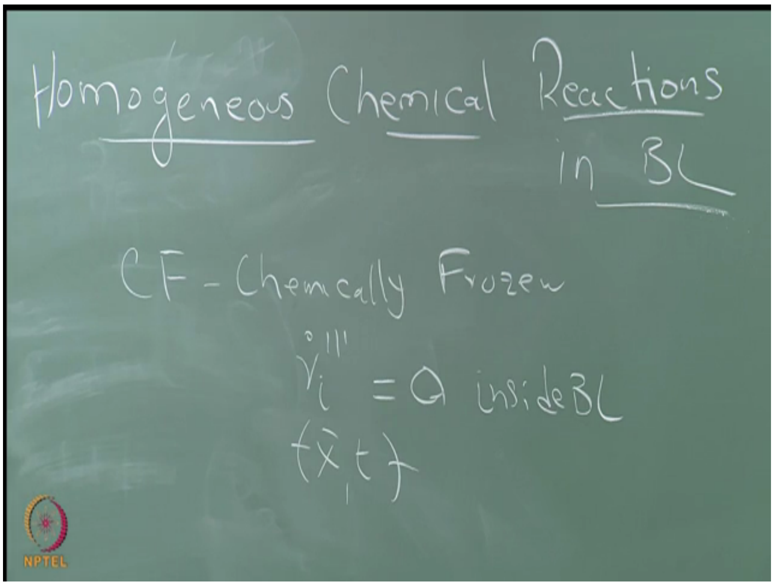

So when we talk about homogeneous chemical reactions in the boundary layer as an analogy breaking mechanism the extreme case called a chemically frozen case which implies essentially that all rates of reaction go to 0 inside the boundary layer this is for all x and t values.

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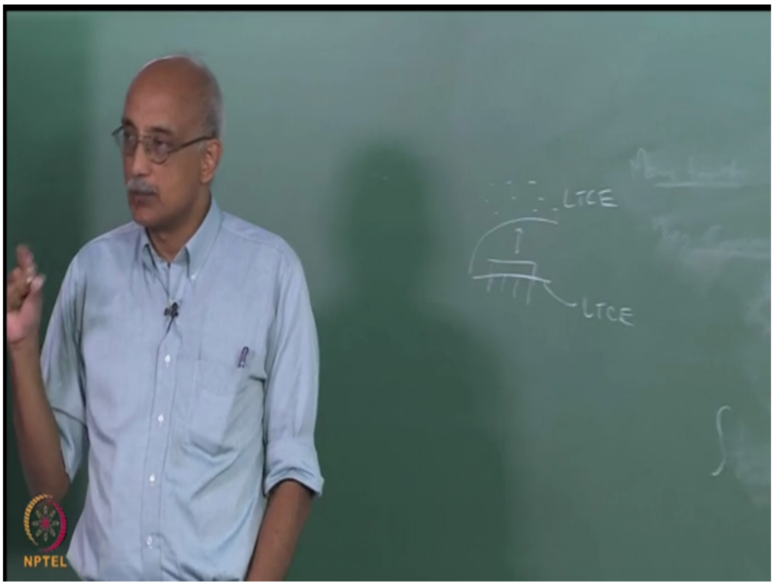

So the reason we do that is simply to make it more tractable from our analysis viewpoint. So essentially they have a substrate on which you are depositing a film and there is a boundary layer that exists on top of this substrate. You are assuming that everywhere above this boundary layer chemical reactions are happening, you can assume that you are reaching chemical equilibrium condition known as LTCE local thermochemical equilibrium.

You can assume that at the substrate also you have LTCE and you can assume that within this very very short distance over which the boundary layer is present, you can assume that chemical reactions are not going to be sufficiently important to affect the mass transfer processes that are going on. So then you make this CF assumption within the boundary layer but clearly the homogeneous chemical reactions are happening and they are happening at a sufficiently high rate this assumption is not valid.

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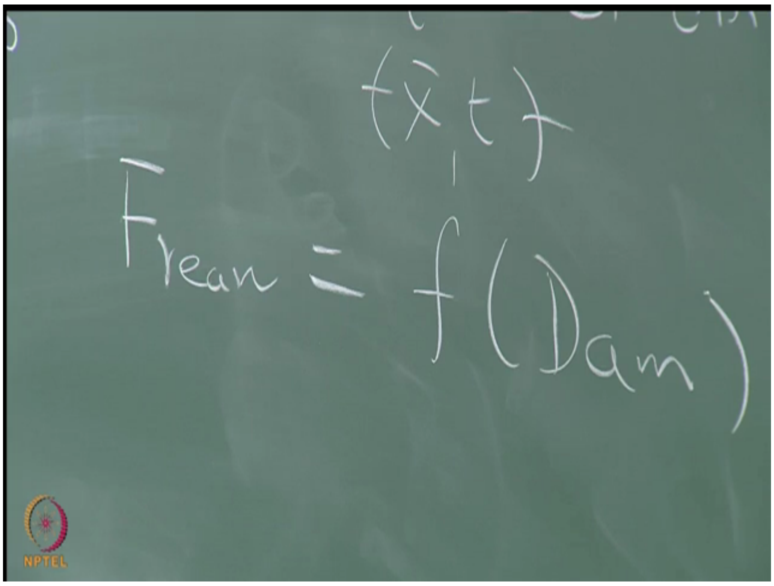

$(\bar{x}, t)$

$F_{rean} = f(Dam)$

So you can define an F reaction which is a correction factor at your applied to the Nusselt number or the Stanton number. So if you remember we can write Num as the F correction factor times Num0 which is the Nusselt number in the absence of that phenomenon and similarly Stm can be written as F times Stm0 and in the case of chemical reactions this F reaction depends on a Damkohler number.

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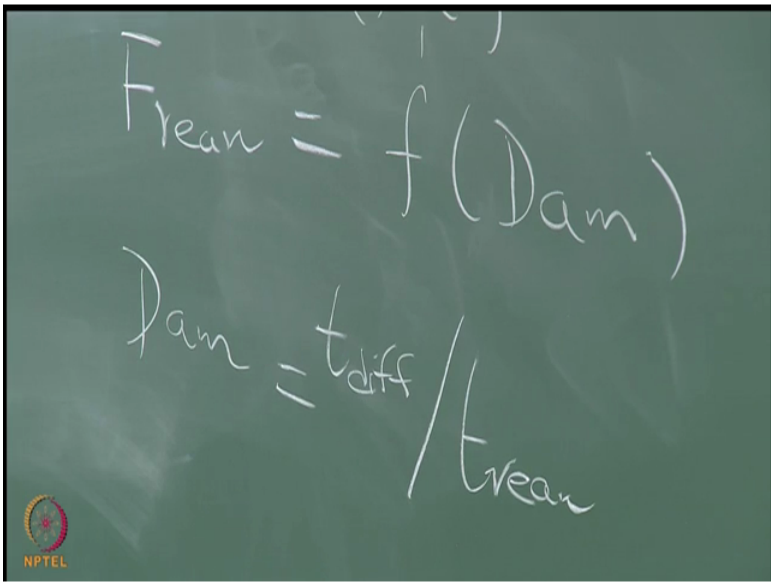

$F_{reac} = f(Da_m)$

$Da_m = t_{diff} / t_{reac}$

Now I am sure you have heard of Damkohler number, right? A Damkohler number is the ratio of what to what? What is the basic definition of a Damkohler number? It measures the ratio between 2 characteristic times, which are characteristic times? It is the other way around t diffusion to t reaction. So in the case of a diffusive deposition process such as CVD the characteristic diffusion time will depend on basically the boundary level thickness and the diffusivity of the species.

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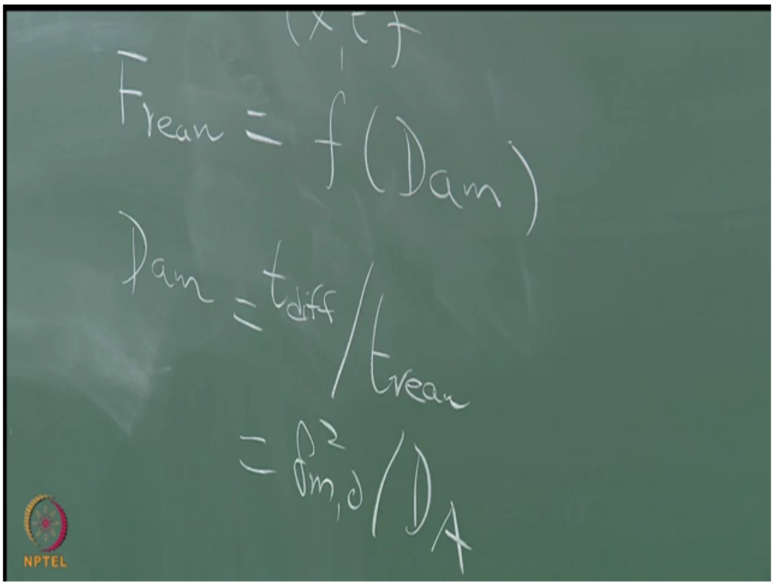

$$\bar{F}_{reac} = f(Da_m)$$

$$Da_m = t_{diff}/t_{reac} = \delta_{m,0}^2/D_A$$

So you can write this as Delta m0 squared over DA where Deltam0 is the thickness of the mass transfer boundary layer in the absence of a homogeneous chemical reactions and DA is the diffusivity of species A divided by reaction time which we can write as 1 over k triple prime where k triple prime is first-order rate constant that has units of one over time.

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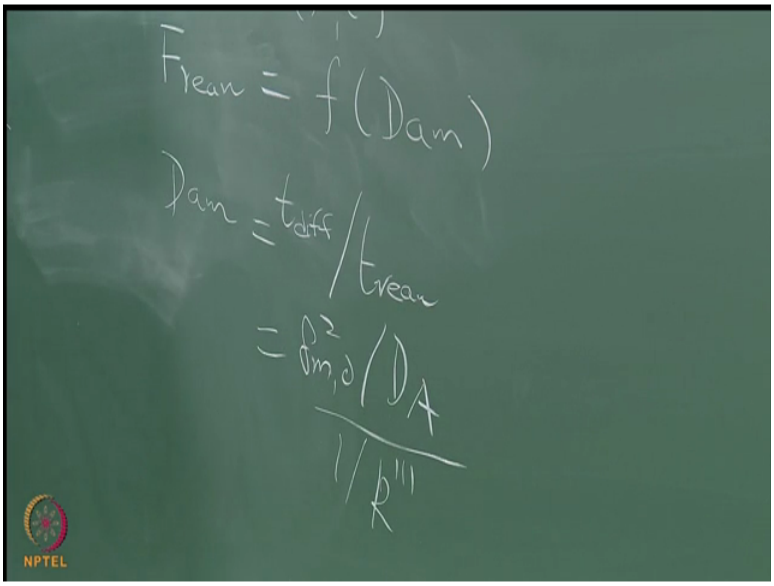

$$\bar{F}_{reac} = f(Da_m)$$

$$Da_m = t_{diff}/t_{reac} = \frac{\delta_{m,0}^2/D_A}{1/k'''}$$

So basically this has units of time and this has units of time.

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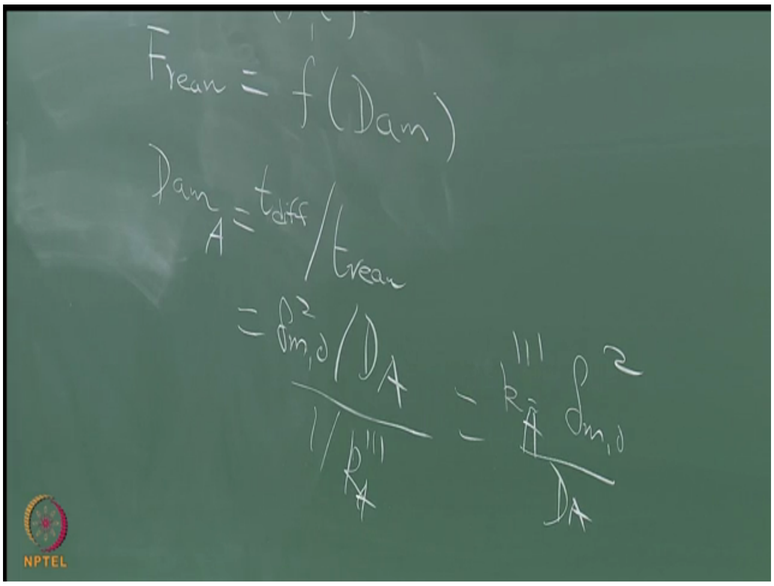

$$F_{reac} = f(Da_m)$$

$$Da_{m,A} = t_{diff} / t_{reac} = \frac{\delta_{m,0}^2 / D_A}{1/k_A'''} = \frac{k_A''' \delta_{m,0}^2}{D_A}$$

Or in other words you can write this as k triple prime times Delta m0 squared over DA because this is also kA triple prime and this is a Damkohler number for species A. So the Damkohler number will be specific for each species that you are looking at. So it is specific to the species under consideration.

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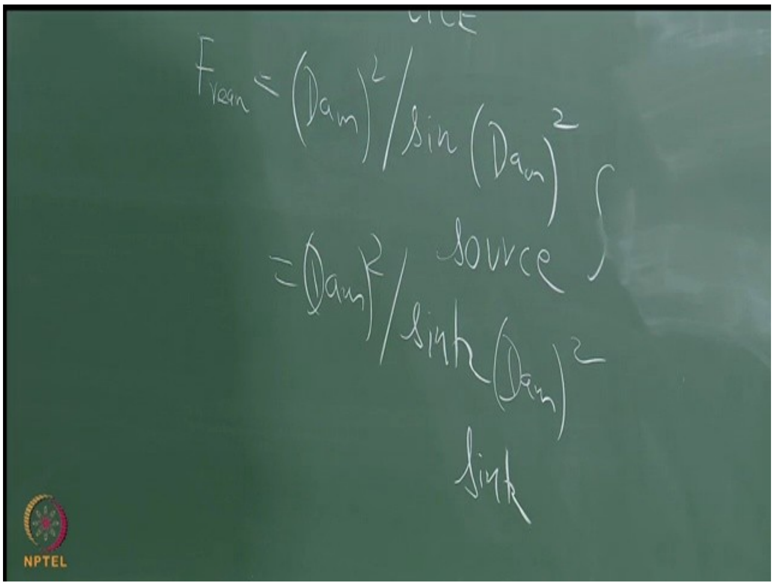

$$F_{reac} = (Da_m)^2 / \sin(Da_m)^2 \quad \text{source}$$

$$= (Da_m)^2 / \sinh(Da_m)^2$$

sinh

So once you have calculated the Damkohler number this way the F factor for chemical reaction can be written in terms of the Damkohler number as Damkohler number squared divided by sine of Damkohler number squared this is for the case where the reaction is a source for the species and you write this as Damkohler number squared divided by the hyperbolic sine, sine h of Damkohler number squared in the case where the reaction is a sync for species A.

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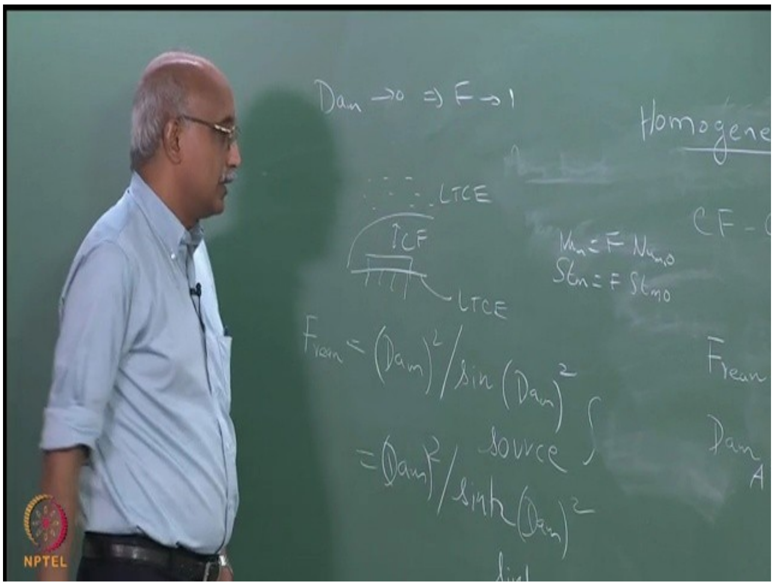

And these terms what they essentially imply is as the Damkohler number goes to 0, what happens to F? F will go to 1, so what does that mean, when you said Damkohler number goes to 0? That means the diffusion time is much shorter than the reaction time, so what does that imply? The reactions even though they may be occurring they are too slow so by the time the reaction happens the species has already diffused and gone to the substrate, so the homogeneous chemical reactions even if they are happening there are too slow to affect the transport process for species A to the substrate, okay. So that is a physical definition.

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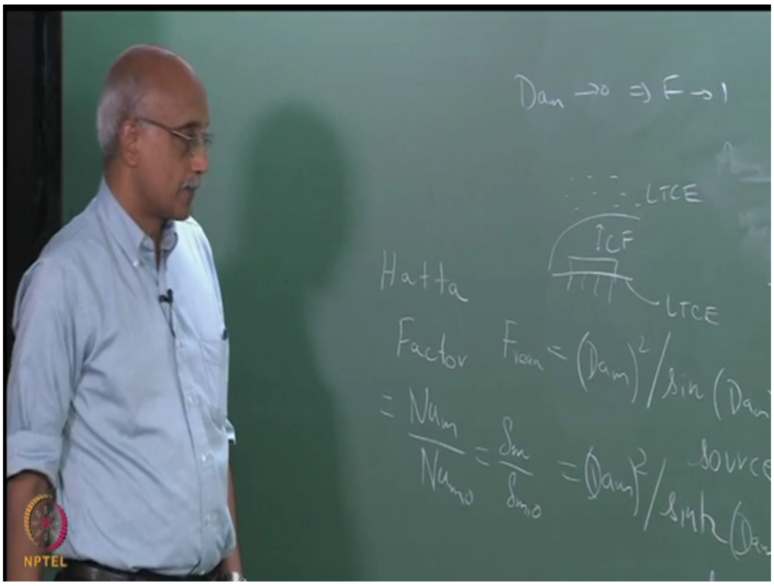

This Damkohler number is also known, actually this correction factor F is also known as the Hatta factor. I do not know if you have heard of that Hatta. Particularly in chemical reaction engineering literature equal talk about the Hatta number all the time. The definition of the Hatta factor of course is, this is equal to Num over Num0 or another way to state this is, it is equal to Delta m over Delta m0.

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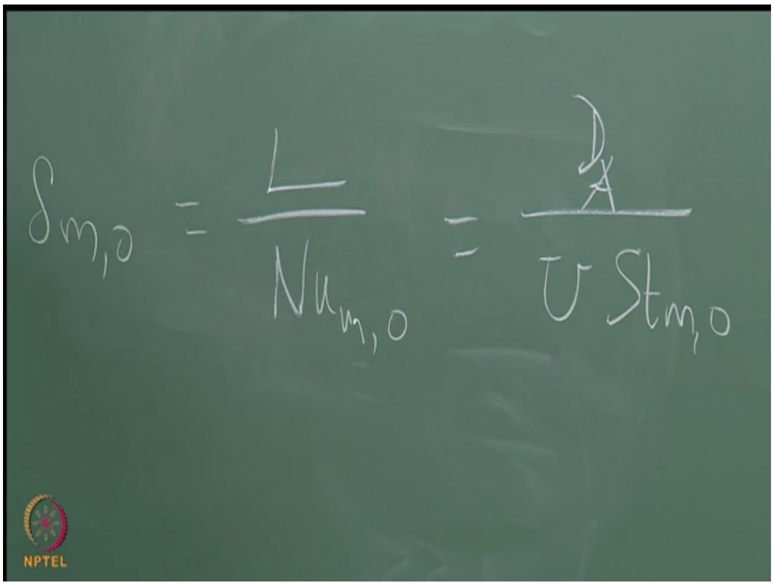

$$\delta_{m,0} = \frac{L}{Nu_{m,0}} = \frac{D_A}{U\, St_{m,0}}$$

And by the way you may recall that previously we had Delta m0 is not easy to measure or to calculate. So what you can do is, you can write this in terms of the characteristic dimension of the system divided by Nusselt number for mass transfer in the absence of homogeneous chemical reactions or in terms of Stanton number can write this as D over U Stanton number, so this will DA.

You can also write this as the diffusivity of species A divided by a characteristic velocity in just like L is a characteristic dimension you could be your approach velocity for example times the Stanton number for mass transfer in the absence of homogeneous chemical reactions.

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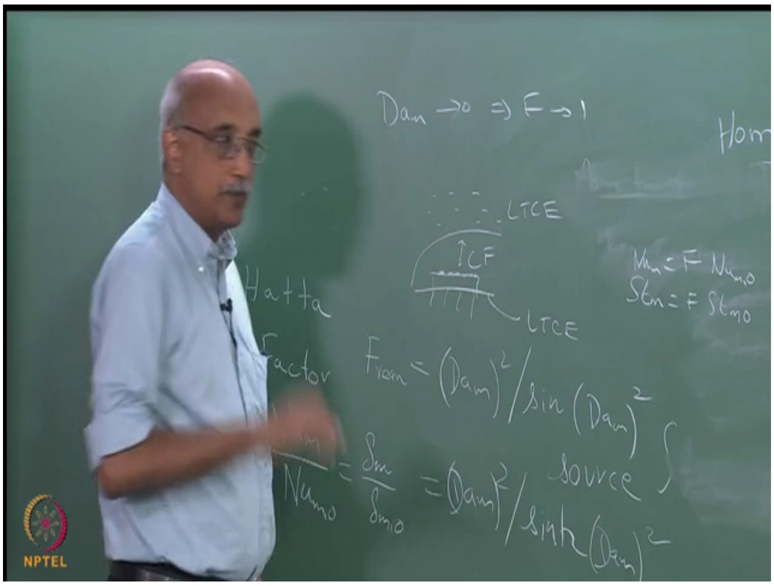

In the case where the only reaction there are happening or heterogeneous chemical reactions either at the substrate heterogeneous reactions will happen right here where the species impact the substrate but it can also happen in the gas phase if you have nucleated droplets of particles in the gas phase. Now if it is a chemical reactions are happening they do not necessarily result in a correction.

So the Nusselt number for mass transfer in the presence of hydrogen as chemical reactions can be assumed to be same as the Nusselt number for mass transfer in the absence of heterogeneous chemical reactions. It is only the homogeneous chemical reactions that introduce this particular correction factor that you call the Hatta factor. However heterogeneous chemical reactions will also be a role play a role in altering the rate at which film formation happens.

The simplest way to look at it is, if you have chemical equilibrium at the substrate then all the corresponding mass fraction values will be at the equilibrium values and the deposition process will happen at its highest rate. However as kinetic constraints comes into play the rate at which material is getting transported to the substrate may remain the same but the rate at which it is getting converted to product will slow down.

So the presence of a kinetically limited deposition process at the substrate results in a net reduction in the rate at which the film grows on the surface. So it is important to look at the effect of heterogeneous kinetic on the deposition process. So what will be the affect of heterogeneous chemical reactions?

Now again there are 2 pieces to it, when you form a CVD film on a substrate the first part is the material getting to the substrate and the second part is the material actually getting converted to a film on the substrate. The rate at which the material is getting to the substrate is what we have previously calculated using Nusselt number and Stanton number.

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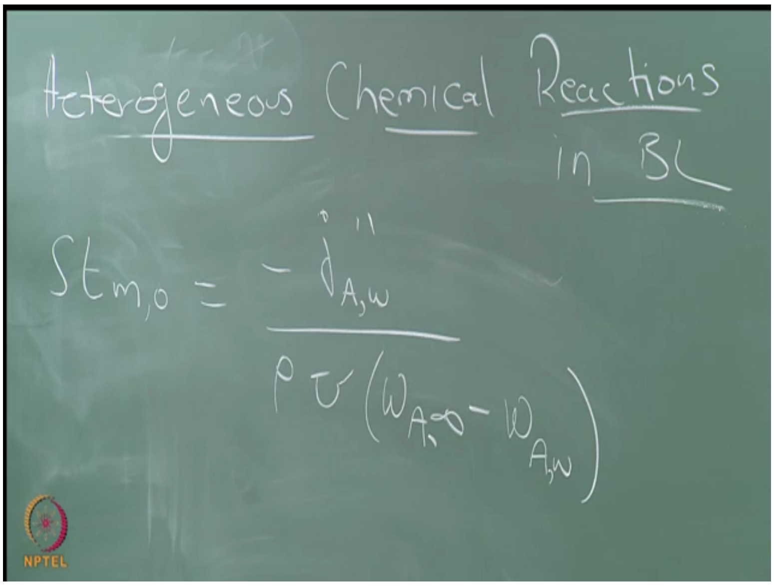

Heterogeneous Chemical Reactions in BL

$$St_{m,0} = \frac{-\dot{j}''_{A,w}}{\rho U (\omega_{A,\infty} - \omega_{A,w})}$$

So our definition of Stanton number says it’s minus jAw dot double prime divided by rho times U times omega A infinity minus Omega Aw, right? Again all this is under let say conditions where the hydrogen as chemical kinetic limitations...

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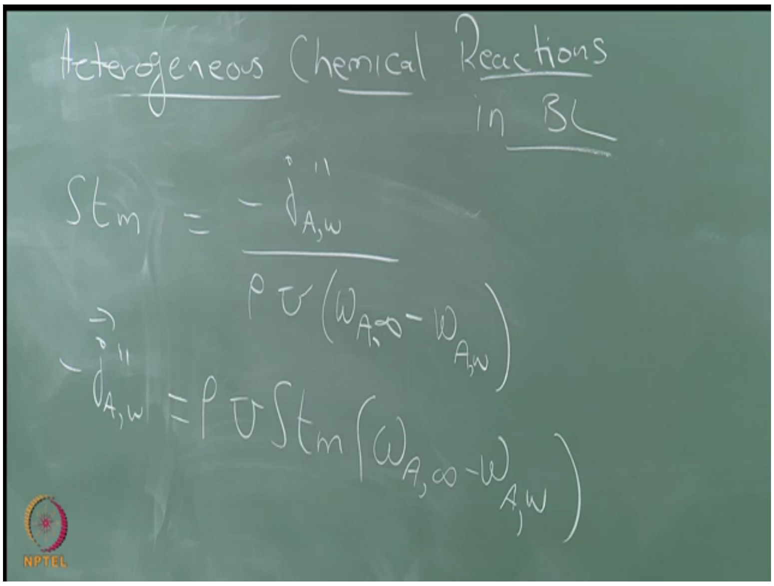

Heterogeneous Chemical Reactions in BL

$$St_m = \frac{-\dot{j}''_{A,w}}{\rho U(\omega_{A,\infty} - \omega_{A,w})}$$

$$-\vec{\dot{j}}''_{A,w} = \rho U St_m(\omega_{A,\infty} - \omega_{A,w})$$

Well actually as far as the diffusion process is concerned it does not matter. So this would be essentially the prevailing Stanton number whether or not there is heterogeneous chemical kinetic constraint at the surface. So we can write the diffusive flux as minus jAw double prime equals rho U times Stanton number for mass transfer times omega A infinity minus Omega Aw where Omega a infinity is the mass fraction of species A just outside the boundary layer and omega Aw is a mass fraction of species A at the substrate and it is this concentration gradient which is driving the so-called reference flux, you know, the denominator is the reference convective flux which basically assumes a linear profile within the boundary layer from Omega A infinity minus Omega Aw.

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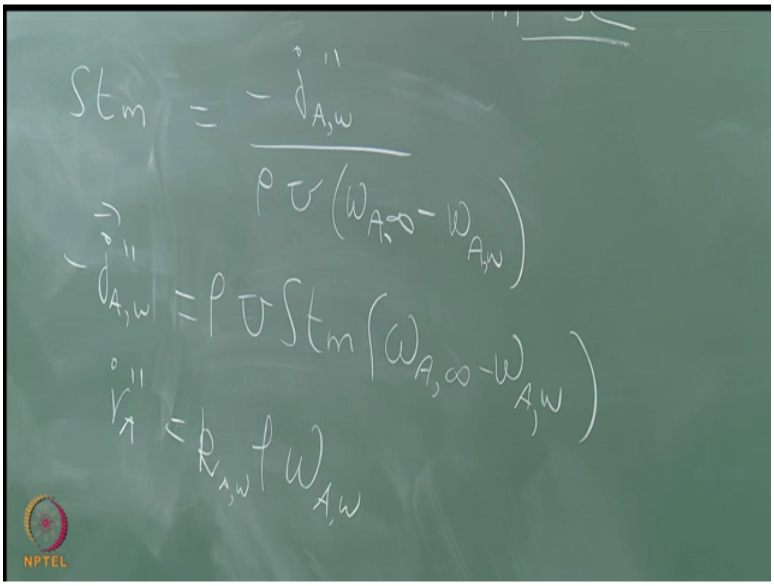

$$St_m = \frac{-\dot{j}''_{A,w}}{\rho v(\omega_{A,\infty} - \omega_{A,w})}$$

$$-\vec{\dot{j}}''_{A,w} = \rho v St_m(\omega_{A,\infty} - \omega_{A,w})$$

$$\dot{r}''_A = k_{A,w}\rho\omega_{A,w}$$

Okay, now what happens when this material comes to the surface? It participates in a chemical reaction and that is a surface reaction. So you can write rA dot double prime equals sum kAw times rho times omega Aw where this is a kinetic rate constant as units of velocity, rho is the density of the gas and omega Aw is a mass fraction of the species A close to the substrate.

So how do you actually calculate the corresponding fluxes here? How do you calculate the values of omega Aw and omega A infinity therefore the deposition flux, you do that by assuming a jump condition at the substrate.

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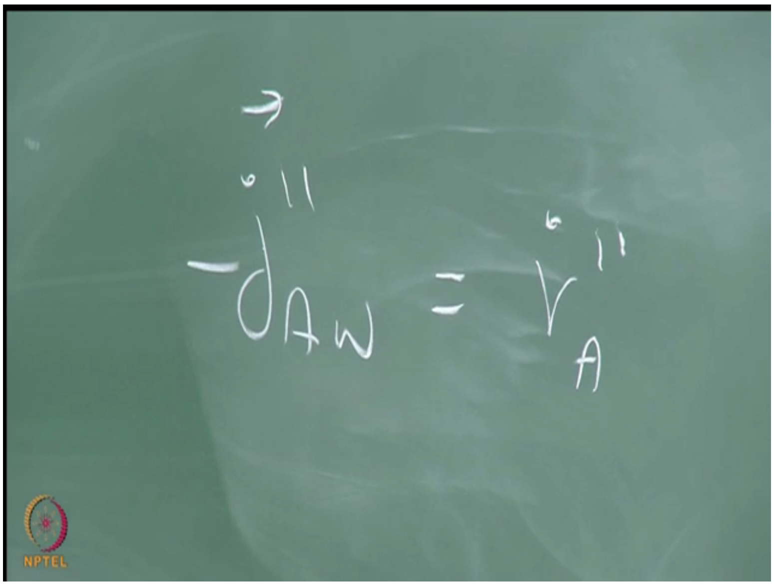

$$-\dot{\vec{j}}''_{Aw} = \dot{r}''_{A}$$

In other words you assume that minus jAw dot double prime equals rA dot double prime. Okay, it is called a jump condition because it establishes and equality between 2 values that exist on either side of the boundary. So when you do that you basically obtain rho times U times Stm Omega A infinity minus omega Aw equals kAw rho omega Aw. So from this you can naturally simplify this.

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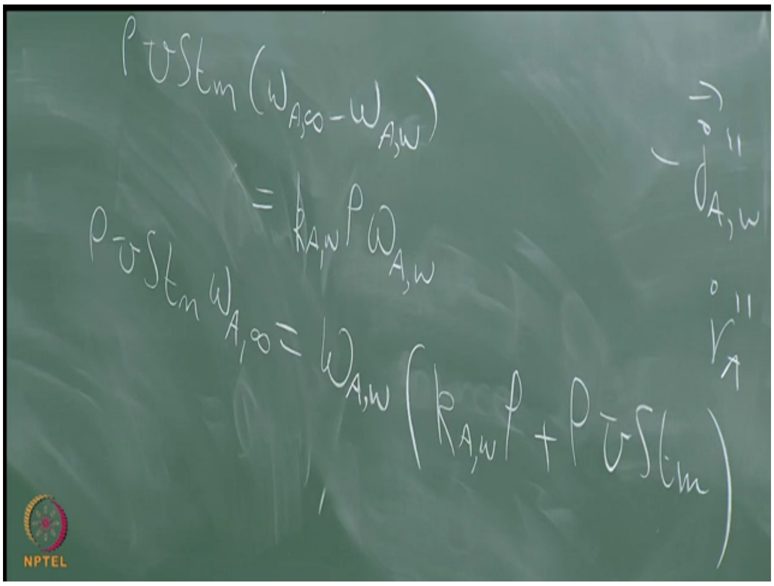

$$\rho \bar{U} St_m (\omega_{A,\infty} - \omega_{A,w}) = k_{A,w} \rho \omega_{A,w}$$

$$\rho \bar{U} St_m \omega_{A,\infty} = \omega_{A,w} (k_{A,w} \rho + \rho \bar{U} St_m)$$

$-\dot{\vec{j}}''_{A,w}$

$\dot{r}''_A$

Let see this means rho U Stm times Omega A infinity equals omega Aw times kAw rho plus rho U Stm, right?

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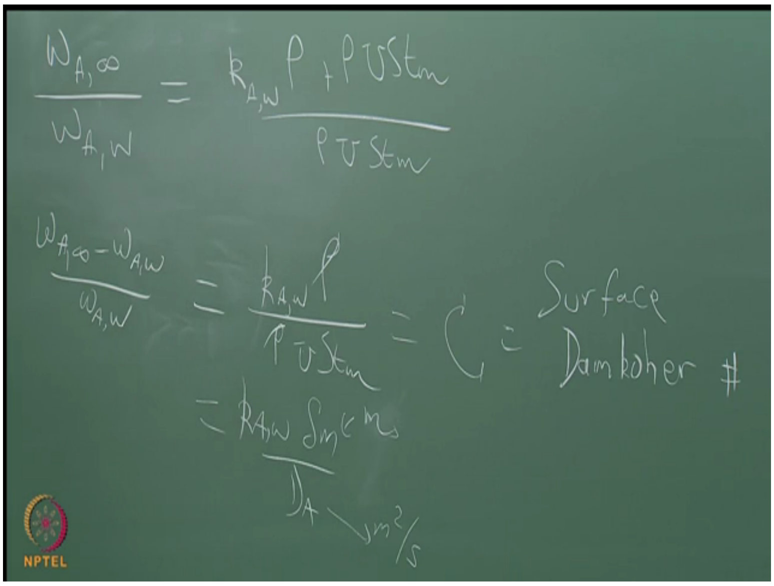

$$\frac{\omega_{A,\infty}}{\omega_{A,w}} = \frac{k_{A,w} \rho + \rho \bar{U} St_m}{\rho \bar{U} St_m}$$

$$\frac{\omega_{A,\infty} - \omega_{A,w}}{\omega_{A,w}} = \frac{k_{A,w} \rho}{\rho \bar{U} St_m} = C = \text{Surface Damkoher \#}$$

$$= \frac{k_{A,w} \delta_m}{D_A}$$

$\leftarrow m/s$

$\searrow m^2/s$

I bring it over to this site this means omega A infinity over Omega Aw equals kAw rho plus rho times U Stm divided by rho U Stm. So if I take this minus 1, so this becomes omega A infinity minus Omega Aw over omega Aw, so this minus1 becomes kAw rho divided by rho times U Stm the rho cancels out. So you obtain omega A infinity minus Omega Aw or omega Aw equals kAw over U times Stm and this is called C which is also known as surface Damkohler number. It is also known as a catalytic parameter.

Hence that sign, the symbol C and by the way we derive this for as a situation where convection dominated the delivery of material to the substrate. You can also write the same thing for the case where diffusion is dominating and then you will obtain kAw times Delta m over DA, so it should have units of divided by velocity, yes, so that is fine. So once you calculate this value of C.

I mean actually if you look at it the Damkohler number in this case is simply that difference between the mass fractions of species A in the mainstream minus the mass fraction at the substrate divided by the mass fraction at the substrate. You can actually now go back and write your diffusive flux expression in terms of that C parameter and if you do the calculation it will come out to C over 1 plus C times rho U times Stanton number times omega A infinity.

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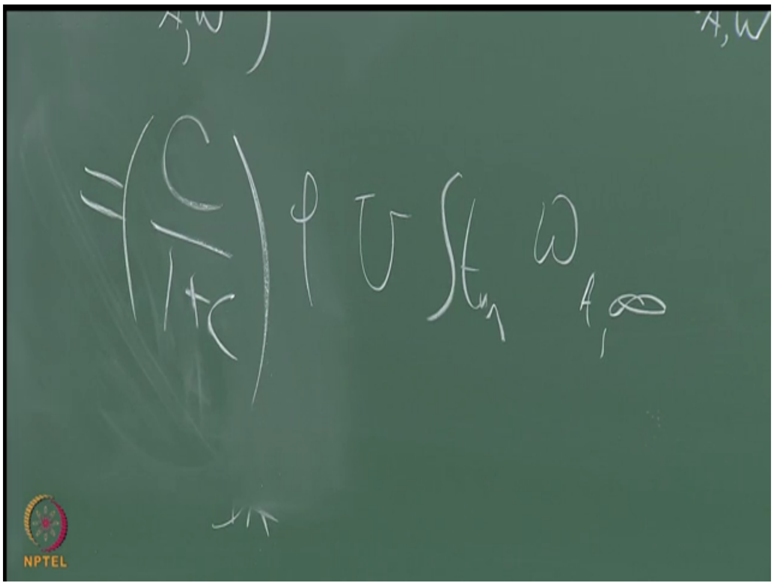

So you can calculate the deposition flux in this case, a simply from the knowledge of the density, the free stream velocity, the prevailing Stanton number and the mass fraction of the diffusing species A in the mainstream of your product gases and you have to know what this parameter is, C parameter and again the C parameter can be estimated in several ways, if you know the mass fraction distribution we can estimate the parameter C.

Or if you happen to know the rate constants at the surface you can calculate the parameter C but the correction factor in this case is essentially this C over 1 plus C parameter, okay. Now what does it mean when we say C is a very small value?

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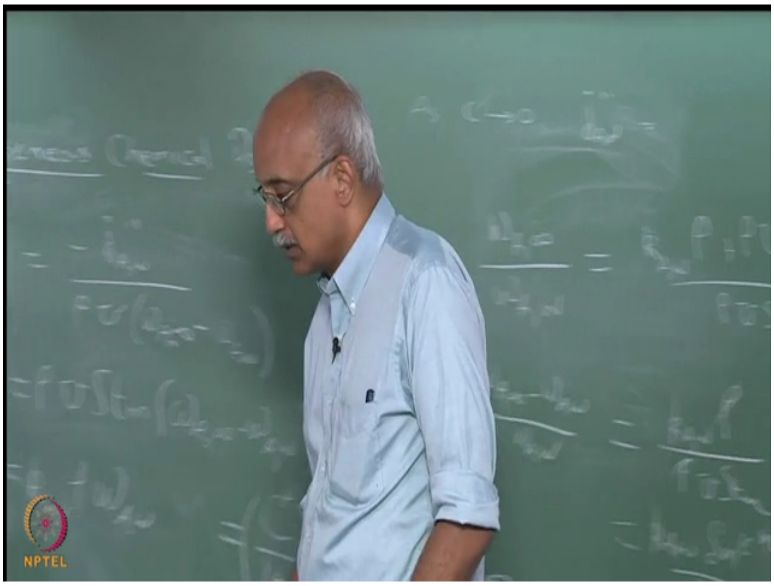

As C tends to let say 0, what happens to the diffusive flux? As C tends to 0 essentially the flux will go to 0 also, right? As omega Aw tends to a very small value, C tends to a very large value. So the smaller the value of Omega Aw the greater will be the diffusion flux do the surface.

So the whole point in a CVD system design should be to keep consuming that species A as it approaches the substrate. As soon as the molecule of species A comes to the substrate must be immediately heterogenously reacted and deposited onto the substrate. So that way, I mean you try to design the process. So that this omega Aw goes as close to 0 as possible. I mean obviously if it goes to 0 essentially you get an infinite deposition rate which is not going to happen but you can certainly keep it as a very small value compared to omega A infinity and that will help enhance the process by which the deposition of film is happening.

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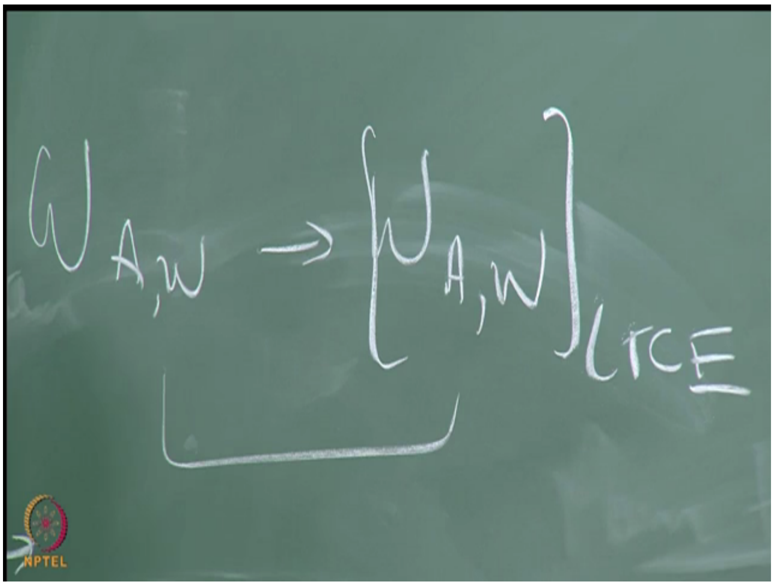

Now in reality the value of omega Aw at the surface is going to assume its equilibrium value local thermochemical equilibrium that is been our basic assumption right from the beginning that chemical equilibrium will prevail both in the CVD reaction system as well as on the substrate on which the deposition is happening. So you can always assume that omega Aw will tend towards its thermochemical equilibrium value.

Of course this is again more likely to happen as Tw increases, the higher the temperature, substrate temperature the more likely that the local mass fraction of species A will tend towards its equilibrium value and typically the equilibrium value of omega Aw is also likely to be its lowest value because equilibrium is achieved not homogeneously but heterogeneously.

At the substrate you have a CVD film that is in contact with the gas, so if you have achieved thermochemical equilibrium and it results in the formation of condensate of species A then obviously its mass fraction and the gas phase is going to be very small because most of the species A ass is going to be in the condensed phase.

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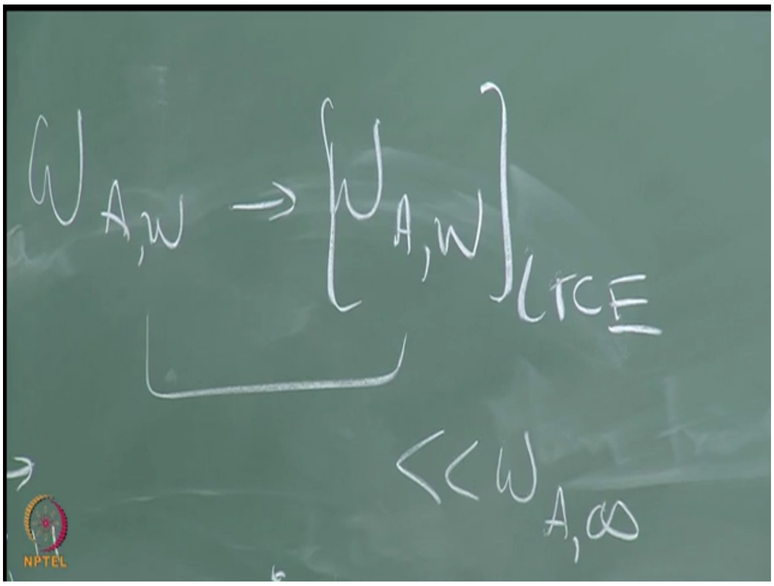

$$\omega_{A,w} \rightarrow [\omega_{A,w}]_{LTCE}$$

$$\ll \omega_{A,\infty}$$

So as long as you drive your process towards equilibrium omega Aw is going to tend towards its equilibrium value which is going to be much much smaller than omega A infinity. Now why would that be? I mean omega A infinity is also an equilibrium value because we are assuming equilibrium is prevailing everywhere except within the boundary layer.

So why would this value be much lower than this, any idea? That is chemical equilibrium prevailing both in the gas and at the substrate but we are saying that omega Aw which is a value at the substrate is much smaller than the value in the gas.

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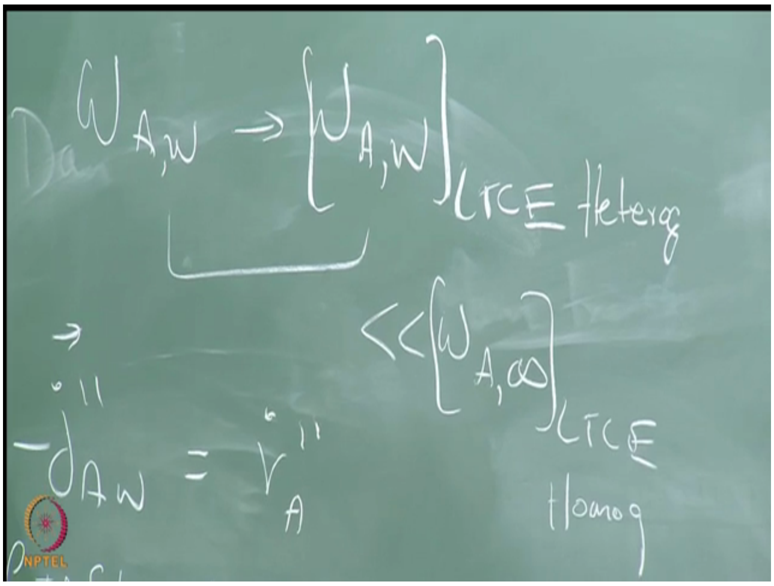

The reason is that this is a homogeneous equilibrium whereas this is a heterogeneous equilibrium. So in the gas they are assuming equilibrium but everything stays in the gas phase, so the mass fraction of the species still has a very high value but at the substrate we are assuming equilibrium applies but it is a heterogeneous equilibrium which means that most of the mass of species A is in the condensed phase.

That is why as long as you drive the entire system towards the equilibrium both in the gas phase as well as near the substrate everywhere in fact except the thin boundary layer your diffusion rates are going to be maximum, the deposition rates are going to be maximum and so on and by the way within the boundary layer I said that one normal assumption we make is, its chemically frozen.

But that is one extreme assumption, for modelling purposes for modelling purposes you can also assume that thermochemical equilibrium prevails everywhere within the boundary layer. Typically that would not affect your deposition rate too much. You know, whether or not boundary layer is chemically frozen chemically reactive what it does do, is added to the complexity of your calculations because now we cannot simply assume that mass transfer across the boundary layer happens only by diffusion.

You have to essentially calculate at each location in the boundary layer, what is the prevailing chemical equilibrium composition corresponding to the local temperature and pressure conditions and so you essentially have to extend your iterative algorithm to include the boundary layer also. The problem with that is inside the boundary layer things change fast, so you have your time steps and your distance steps have to be much shorter.

So the assumption of chemical reactions happening inside the boundary layer whether an equilibrium condition or not significantly extends your calculation time because the complexity of characterizing what happens within the boundary layer is much greater than the complexity of characterizing happens outside the boundary layer because outside the boundary layer you do not have to deal with so many gradients, you know, it is almost uniform condition in a design CVD reactor but inside the boundary layer by definition things change rapidly.

And so, you know, just from the complexity viewpoint we typically prefer to make the assumption the boundary layer itself is chemically frozen and there are no chemical reactions going on. So this is fundamentally the way you incorporate homogeneous kinetic as well as heterogeneous kinetic into your diffusion deposition model and I think that pretty much brings us to the end of this module where we have been looking at the effect of transport phenomena CVD rates.

By now you should have a reasonably good picture of how to approach the problem to obtain the prevailing rates of deposition and growth of the film. We have to follow a very systematic procedure where you start with known, the only known things that you have or the temperature distribution on the outer walls of the CVD reactor, the temperature of the substrate and the pressure that you are applying to the reactor and your input parameters.

What is your feed gas? What is the concentration of your reacting species in the feed gas? That is pretty much it, from that you have to be able to apply all the principles that we have talked about, the thermodynamic principles as well as the transport principles to estimate an associated rate at which deposition is happening on the surface resulting in the growth of the film.

It is not a sequential process, it is an iterative process because you know the prevailing velocity distributions and temperature distributions affect your mass fraction distribution but with that the mass fraction distributional itself can also affect your velocity distribution and your temperature distribution. So it is a highly coupled process which has to be solved iteratively.

The other thing that you have to give in mind is the stoichiometry of the film has to be consistent with the associated transport rates you cannot violate the elemental flux ratio condition that we have talked about. If you are forming, you know, Si3N4 film then the molecular flux of Si2m has to be in the 3 to 4 ratio. Otherwise you are violating the stoichiometry of the film.

So that can introduce us an iterative step into your process, you have to calculate diffusion rates assuming a certain thermodynamics at the surface and then once you that if the fluxes that you calculate are not in the right ratio, you have to iterate until you achieve a self consistent solution which satisfies the thermodynamic constraints as well as the transport constraints.

And you have to provide when you are calculating the transport rate which directly corresponds to the rate at which the film is growing, you have to ensure that you apply all the appropriate correction factors. You have to understand whether or not mass transfer analogy condition holds and if it does not what are the correction factors that you have to apply to the Nusselt number and Stanton number in order to obtain the actual prevailing Nusselt and Stanton numbers and use those to calculate your actual prevailing deposition rates.

So there is lot of work here for the chemical engineers to do and there is a reason why CVD processes in general employ a lot of chemical engineers in the industry. Without a good understanding of chemical engineering phenomena involved it is very difficult to design an efficiency CVD system.

Okay, so what will do in the subsequent classes is, go back to looking at some practical CVD systems. So we will start with CVD reactors that are used for making silicon films and we will also look at some CVD reactor that are used for making metal films and semiconductors and so on and as we discuss these specific systems we will refer back to this module, the transport model because that is going to be, you know, obviously crucial in our discussions in the following classes as well.

Okay, so any questions on what we have covered today or about transfer process in general in CVD systems?

“Professor -Student conversation starts”

Student: Sir the valley you have calculate it, the inside that omega distinguish…

Professor: You can I mean once you know the temperature and once you know the pressure…

Student: Experimentally it is not possible.

Professor: Experimentally it is difficult but there are instruments that can do it, you know, the difficulty is doing it (()) (45:57). You can always draw a sample of the material and do off-line analysis. For example you can check out some vapours and gases dissolved in a liquid and then analyze the liquid you can take the gases directly through a gas chromatography and analyze.

The real problem in CVD reactors is how do you do the (()) (46:18) without having to suck out the material, that is more difficult to do.

Student: basically another is not also possible like…

Professor: Velocity you can always measure, you can have instrumentation inside to measure, you know like in anemometer or something that can measure the velocity distribution inside. The most difficult thing to measure out is the mass fractions, particularly when they are at very low concentrations because you are talking about 10 to the power minus 6 and smaller values, parts per million parts per billion values, so it is difficult to measure.

Okay, see you at the next class.

“Professor-Student conversation ends”