Chemical Engineering Principle of CVD Processes Prof. R. Nagaranjan Department of Chemical Engineering Indian Institute of Technology Madras Module-2 Lecture 18 CVD Transport Phenomena: Mass Transfer Analogy Condition (MTAC)

Good morning and welcome to the next lecture in our course on chemical engineering principles of CVD process. In the last lecture we looked at the mass transfer equation and a little more detail there are essentially 3 contributions to mass deposition fluxes in a chemically reacting flow system such as CVD reactor and basically convection, Phoresis and diffusion and we spent a little bit time looking at how all 3 of these contributions can be incorporated into the mass balance equation.

And also how Phoresis in particular can be expressed in terms of a characteristic Phoretic velocity as well as a Phoretic force and a friction coefficient and then we also define certain dimensionless numbers in particular the Stanton number, the Nusselt number and the capture efficiency which can be used to effectively represent our results as well as present the data in a way which is comparable across reactors and so on.

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Now as we were deriving these equations there was one key assumption which we made which is that the diffusing species is present in trace amounts. In other words any of the diffusing elements A which we assumed at its much smaller than 1 and while this is a good assumption in most CVD systems there are situations where this can be violated, so we need to look at how the Nusselt numbers and Stanton numbers that we derive for the dilute species case will change when you have a non-dilute species diffusing in your system.

And also in any physical system the easiest parameter to measure is temperature. So if you look at mass momentum and energy conservation, the 3 corresponding feel density parameters are mass fraction, merger and velocity but from an instrumentation viewpoint temperature is much easier to measure than either mass fraction of species or prevailing velocities in the system.

And so ideally what we would like to do is map the temperature distribution in a CVD reactor and from that be able to estimate the prevailing distribution of velocities as well as of mass fractions of the various reacting species.

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Now in order to be able to do that we have to have a condition that is known as the mass transfer analogy condition or MTAC. This condition when satisfied enables us to take temperature distribution data in non-dimensional terms and from that extract corresponding distribution data for reacting species concentration.

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For example if we were to express the temperature distribution in a CVD reactor as sum Tw minus T over Tw minus T infinity where again the designation represents how close you are to the substrate.

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So in a CVD reactor where you have a substrate which is heated, a substrate temperature is what we call Tw and the temperature that is far away from the substrate is what we represent as T infinity. So the temperature at any location particularly within the boundary layer and by the way most of our concentration will be in this region which is the mass transfer sublayer or

boundary layer around the substrate because there is really bad the deposition processes are happening.

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So we want to calculate the temperature at any location within this boundary layer you can obtain it as, in this fashion you can write as some non-dimensional variables T star which will be a function of non-dimensional distance, non-dimensional times, Reynolds number and Prandtl number. So we know sufficient key transfer theory and we know how to measure the temperature sufficiently well to validate our theory.

So we can always derive an equation of this form, so this may be for example it could be that this may be Reynolds number to the power half, Prandtl number to the power 1 3rd, right for some dependency like that. So let us assume that we know how to derive this, we know how to characterize the temperature distribution within the laminar sub layer surrounding the substrate in a CVD reactor.

And by the way this is for the case where force convection is dominant you can also write this as T star of X star T star Rayleigh number and Prandtl number in the case where natural convection is dominant. Again the star simply represents that they are non-dimensional values corresponding to the specific parameters.

Of course the Rayleigh number this is defined as g beta delta T L cube, actually for a define Grashof number, are you familiar with Grashof number and Rayleigh number? So they are used to represent just like Reynolds number is used to represent the ratio between convection and diffusion in a force convection system. Similarly the Grashof number is used to represent the ratio of convective transfer to diffusive transfer for a natural convection system.

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So here g is the body acceleration, beta is the coefficient that are present change in density as a function of temperature while holding key and omega a constant, delta t is your temperature differential, so in this scale it will be T infinity minus Tw, L is the characteristic dimension in your system and mui of course is the kinematic viscosity, mui by rho.

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Now if we take this Grashof number and by the way this is a Grashof number for heat transfer, so you represent it with a subscript h, from this you can derive a Rah which is Grashof number multiplied by the Prandtl number and the Rayleigh's number is what you substitute into this equation. So whether it is forced convection dominated or natural convection dominated you can obtain the temperature distribution both theoretically as well as experimentally.

Now the question is how do you go from there to estimating the mass fraction distributions inside the reactor? In other words what you would like to be able to do is similarly write omega Aw minus omega A divided by omega Aw minus omega A infinity is equal to sum omega A star which is a function of omega A star which is a function of X star, t star and Reynolds number and Schmidt number or in the case of forced convection this will be Rayleigh number for mass transfer, Schmidt number and by the way the Rayleigh number for mass transfer would essentially have instead of delta t you would have delta in the mass fractions instead of defining beta and again this is a beta h let us call this, you can define beta m which would be representing the ratio of delta rho with respect to change in mass fraction.

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Actually why do not we rewrite in the case of natural convection for mass transfer corresponding Grm value would be equal to G times beta m times Delta omega A times L cube over U square where Beta m equals minus 1 by rho of del rho by del omega A holding pressure and temperature constant and Rayleigh number of mass transfer would then be equal to Grashof number for mass transfer times the Schmidt number.

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So we essentially substitute Schmidt number for Prandtl number, so let say that you want to write similarly the mass fraction diffusing species A at any location inside the boundary layer in this non-dimensional form.

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So you need to know what is this omega A star as a function of X star T star and the prevailing convective and diffusive dimension numbers. If you could see that these 2 are identical, in other words if you can take the this function which you know and simply substitute for the Prandtl number that Schmidt number in this case and in the case of natural

convection substitute Rayleigh number for mass transfer in place of the Rayleigh number for heat transfer.

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If the same expression would then apply for example if T star goes as Reynolds number to the power half and then lumber to the power 1 3rd, if you can from that derive that omega A star will go as Reynolds numbers to the power half, Schmidt number to the power 1 3rd then you can essentially take the functional value that you have derived for how the dimensionless temperature is distributed.

And simply extract from that does by making the appropriate substitution the distribution of the mass fraction. If you could do that obviously it greatly simplifies our ability to simulate the system and it eliminates a need to actually measure the concentrations in the system. However it turns out that in order for this analogy, this mass transfer analogy to hold, there are certain requirements, one of them is that the mass fraction of the diffusing species must be in traced quantities.

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The second one is that the Phoretic forces must be absent. In other words there should be no external field which is operating on the particular species and causing its mass transfer to happen and the third is that there should be no homogeneous reactions in the boundary layer. Now the reason for these 2 conditions is that, in order for the analogy to hold what that implies is whatever external force or phenomenon there is, it must act identically on both mass transfer and heat transfer.

For example diffusion is essentially the mechanism is the same whether you are talking about heat transfer or mass transfer or even if you talk about convection the way that heat is transported convectively is very similar to the way mass transported convectively? However if we take Phoresis force for example gravity the effect of a gravitational field on mass transfer is obviously very different from its affect on heat transfer.

 So when gravitational field is significant in your system you cannot use the mass transfer analogy or for example thermophoresis, it basically refers to the effect of temperature gradient on mass transfer. So clearly there is no equivalent of act for heat transfer, you cannot talk about the effect of temperature gradient on heat transfer because that is already covered under you know Fourier launch so forth.

So the presence of any Phoretic field violates the mass transfer analogy condition and similarly you know within this boundary layer adjacent to the substrate we like to assume from a modelling viewpoint that the gas phase reactions are essentially frozen. In other words all the chemical reactions are occurring outside the boundary layer and then they occur at the

surface in heterogeneous fashion but in general for modelling purposes it is assumed that within that diffusion boundary layer which is very very thin we neglect homogeneous chemical reactions.

That enables us to apply the mass transfer analogy conditions but again imagine if you are allowed homogeneous reactions to occur in the boundary layer clearly that affect on mass transfer will be very different than their effect on heat transfer because the way homogeneous reactions affect the mass fraction profile in the boundary layer will be very different from their effect on the temperature profile within the boundary layer.

In general their effect on the mass fraction gradient will be much stronger, essentially species could be appearing and disappearing within the boundary layer due to homogeneous chemical reactions that corresponding effect on the heat transfer will be very muted. So there is again no clear correspondence between the 2. So these are 2 conditions you need to bear in mind when you are trying to apply the mass transfer analogy condition.

So we will look at the effects of all 3 of these conditions what happen when omega A is not much less than 1? What happens when Phoretic phenomena are not negligible? And what happens when homogeneous reactions are occurring and how that affects your deposition characteristics? Before we do that just a quick comment, so far we have been focusing mostly on the energy to mass transfer analogy.

Now the master momentum transfer analogy is actually a lot more complicated it is not as easy to apply because momentum transfer particularly in the case where there is a pressure gradient along the direction of flow the mechanism tends to be very different between momentum transfer and mass transfer. So the analogy in that particular case is not as obvious.

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However in the limiting case where there are no stream wise pressure gradients, there is one analogy you may be familiar with Chilton Colburn analogy which says St the Stanton number for mass transfer equals Cf by 2 times Schmidt number to the power minus 2 3rd, so this is an analogy that people have used but again because it has very limited validity, it requires that along the direction of flow there cannot be a pressure gradient which is a hugely limiting assumptions.

But when the assumption is valid then if you can measure skin friction coefficient which is not a difficult measurement from that once you know that distribution of the skin friction coefficient around an object you can from that evaluate or estimate the effect of or the associated distribution of the mass transfer Stanton number around the object but in the case of the Nusselt number there is no well-known analogy that people have been able to establish.

So the only mass to momentum transfer analogy that is reported in literature and in textbooks is the Chilton Colburn analogy that says the Stanton number for mass transfer equals its related to the skin friction coefficient and the Schmidt number. Okay, so let us take these 3 cases in sequence not dilute species transfer, Phoresis phenomena and homogeneous nucleations in the boundary layer and look at their effects.

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So the first case when omega A is not equal to or is not much smaller than 1 physically what does that imply? CVD happens because you have a substrate with the boundary layer around it and mass transfer is occurring from the outside of the boundary layer to the substrate, right? Now there is a diffusive transfer but it is a net transfer of material from the fluid to the substrate.

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Now typically in the case of, by applying mass conservation principles this assumes that there would be an equal and opposing flow which will essentially negate the diffusive flux towards the surface. Now we tend to neglect this flow in general because the diffusing species or a trace amongst, so the flow that is associated is not large enough in magnitude for us to worry about it.

However as Omega A the mass transfer of the depositing species becomes comparable to 1 which will be the case where you do not use a carrier gas or (0) (21:23) in the CVD system. If you are using for example pure SiH4 as you are depositing species and you are making Sinh2 that will be a case where SiH4 concentration is close to 1 and so you cannot say that it is much smaller than 1.

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Now in that case you have to take into account the flow that opposes the diffusive flow and that is called Stefan flow and it has a definite effect on the mass transfer characteristics in the system.

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It is typically represented by a parameter Bm which is written as Vw times delta m over DA where Vw is the velocity associated with this opposing flow. So it is the velocity, you are taking the mass flux that is resulting and converting it into a velocity by dividing in appropriate density.

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So essentially Vw is a velocity representation of the Stefan flux that happening. Delta m is the thickness of the mass transfer boundary layer in the presence of Stefan flow and DA is the diffusion coefficient of species A, the effect of this flow is to alter the Nusselt number. Let say Num, A,0 is the Nusselt number in the absence of Stefan flow and some NumA is the Nusselt number in the presence of Stefan flow then these 2 are related by NumA equals NumA0 times a correction factor due to Stefan flow.

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And this correction factor f in the case of Stefan flow is related to this parameter Bm as ln of 1 plus Bm over Bm, so the effect of Stefan flow is to reduce the rate of deposition to the system there are cases where this Vw can actually enhance deposition as well for example if you have a perforated substrate and you are actually sucking air through the perforations, you can actually use this flow to enhance the rate at which deposition is happening to the substrate.

In that case the Vw a negative factor and the correction factor f will be greater than 1 but in general whenever you have diffusion happening towards the substrate and using a convective flow which balances it, the convective flow has effect of taking some of the depositing material back to the mainstream and thereby reducing the net rate of deposition that is happening.

Another way to represent this is in terms of what is called the bio number, the bio number has representation that is very similar to Bm but with a very subtle difference, it is actually written as Bm deltam 0over DA, the difference between the 2 is in this term, the Bm parameter which is also called the blowing parameter uses the boundary layer thickness with Stefan flow in the numerator whereas the bio number uses the boundary layer thickness without Stefan flow in the numerator

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When you write the bio number in this fashion you can also write this as Vw times a characteristic dimension L over DA times Nusselt number again in the absence of Stefan flow in the denominator, so it is basically another representation of the bio number, in the case where you have convective flow being the dominant effect you can also write the bio number as Vw over a characteristic velocity U times Stanton number for mass transfer again under non-Stefan flow conditions.

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So these are various definitions of the bio number and depending on whichever is the dominant flow mechanism as well as your ability to measure the various parameters here you can choose to use any of these definitions of the bio number or you can simply use the definition of the blowing parameter. The blowing parameter is something that is unique Stefan blowing but as we will see later the bio number is something that is common to any process that causes a difference in the transport flux.

So once you have estimated this bio number, let us call that Bim, A the correction factor now f Stefan comes BimA divided by 1 minus exponential of minus BimA, so you can estimate the correction factor using either the formula for the blowing constant Bm, it should actually be Bm, A, delta m, A or you can write the correction factor in terms of the bio numbers in either case once you have estimated the correction factor you take the Nusselt number that you have defined in the absence of Stefan flow and multiplied by the correction factor to get the actual prevailing Nusselt number from that then you can derive the actual prevailing deposition rate film thickness and so on.

Now the reason we say that Stefan flow does not violate mass transfer analogy condition is because Stefan flow actually affects both mass transfer and heat transfer identically. So just like we have defined BmA, we can also define BhA which is the blowing parameter corresponding to heat transfer as Bw delta h over Alpha A or Alpha where Alpha equals k by rho Cp.

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So you can substitute for mass diffusivity by thermal diffusivity, you substitute the boundary layer thickness for mass transfer with the boundary layer thickness for heat transfer and you can estimate Bh and once you have that you can again derive a correction factor for F Stefan in the case of heat transfer as ln of 1 plus Bh over Bh.

Or in terms of the bio numbers again you can write, in the case of a transfer you can write a bio number for heat transfer under Stefan flow conditions as Vw delta h 0 over Alpha and again it and write this as Vw times L over Alpha times Nusselt number for heat transfer under no Stefan flow conditions in it and write this as Vw over U times Stanton number for heat transfer under normal or nominal conditions.

Yes Vw as I was explaining is the representation of this opposing flux using a velocity, so basically rho times Vw will give you the Stefan flux, there is a flux associated the diffusive transfer of the condensing species to the surface which is being approached by another flux in an equal and opposite direction, so once you know what that flux is any know the density can estimate the velocity corresponding to that.

So the point is this Fh correction factor that you have for Stefan flow is identical in its form for both heat transfer as well as mass transfer and therefore the correction factor will apply equally to both. Hence the mass transfer analogy is not violated, okay.

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Now let us take another case which is Phoretic transfer. So in the case of Phoresis, our definition of its effect is very similar to what we just did for Stefan flow. So you will take the Nusselt number for mass transfer in the presence of Phoresis divided by the Nusselt number for species A in the absence of Phoresis and write this as a correction to F Phoresis where again this F Phoresis will be related to a bio number for Phoresis divided by 1 minus exponential of minus bio number.

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Where again this bio number will be defined similarly as, now in this case instead of VW we simply use the associated Phoretic velocity, you remember yesterday we defined for ridiculously in the case of sedimentation, Phoretic velocity in the case of electrophoresis, Phoretic velocity in the case of thermophoresis and so on.

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So you simply take the corresponding velocity parameter C and multiplied by Delta m0 over DA and everything else applies you can again write this as C times L over DA times Num0 of A can write this as C over U times Stanton number for mass transfer in the absence of Phoresis and so on. Now Phoresis as a correction factor can be positive or negative depending on which direction the Phoretic force acts.

If the Phoresis is such that it pushes the material towards the substrate then it will enhance deposition rate for example in the case of thermophoresis, if the substrate is hot and the reactor walls are called which is a normal condition thermophoresis tends to happen from hot to cold, so the Phoretic flux will oppose the deposition flux, so you will see a net reduction in the CVD rate when thermophoresis is happening to a significant extent.

However even this is only true if the diffusing molecule is heavier than the carrier gas, when the diffusing molecule is heavier than the carrier gas it tends to go from high-temperature to low-temperature when you applied a temperature gradient. If the diffusing species is lighter than the carrier gas then it happens in reverse. However as you know in most CVD reactors the carrier gas tends to be a light gas like helium or hydrogen or species like that.

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So typically the diffusing species will be heavier than the carrier gas, so the effect of thermophoresis will typically be to take the material away from the surface and thereby reduce the effective diffusion rate which means that F Phoresis will be typically less than 1 then the case of thermophoresis. In the case of sedimentation if the reactor configuration is such that sedimentation helps the deposition process for example in the stagnation flow configuration then this can be greater than 1.

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But it also requires that the diffusing species must be heavy enough that gravity does become a significant effect. So it depends once again on the nature of the deposition process how heavy is the depositing molecule? but in general you would say that this will be greater than 1 for gravitational effects.

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Now for other 4 field forces like electrophoresis that is totally up to you for example you can actually design a CVD reactor where the electrophoretic field is oriented in such a way that it either enhances the rate of deposition or reduces the rate of deposition. So depending on the design can be greater or less than 1 for an electrophoretic field or for a magnetophoretic field there is also a Phoretic feel called Diffusiophoresis which by the way simply another name for Stefan blowing. It is the Phoretic flow associated with diffusive flow, okay.

So the Stefan flow example we looked at first is actually a subset of Phoretic flows. However with a key difference as it mentions the fun flow acts on both mass transfer and heat transfer in an identical fashion, so it does not violate heat transfer analogy conditions. However the other Phoretic phenomena do have a significantly different effect on mass transfer compared to heat transfer.

So in all these cases the heat transfer analogy condition is violated which means you cannot take T star is being equal to omega Astar, T star of Re, Pr cannot simply take that and rewrite it with Reynolds number and Schmidt number and assume that the same non-dimensional formulation (()) (39:41). Another way of saying it is a Phoretic phenomena or important in your system and you want to know the species concentration distribution in the system you do not have any other option but to actually directly instrument for it and measure it.

You cannot simply measure the temperature distribution and assume that the concentration dissipation will follow the same pattern, okay. So is Phoresis something to be desired are not in a CVD reactor? It is certainly complicates your simulations it complicates your measurements, on the other hand if Phoresis can be controlled properly it can enhance your deposition rate mostly that is what you are looking for.

Now if you are running a CVD reactor your intent is to get as much material to deposit and as shorter time as possible. So Phoresis does give you a handle to do that, however just remember that its effects are difficult to predict and difficult to measure, it is somewhat empirical people usually do it in a trial and error cases, so they would apply an electric field see what it does to the deposition rate, if it helps they will continue to apply it, if it does not seem to help or if it is actually making it worse than they will stop using it.

But if you know chemical engineering principles, if you understand these phenomena these effects if you understand then you can apply the mass transfer analogy condition and when you cannot if you understand how to take your baseline Nusselt numbers and Stanton numbers and correct them for the prevailing Phoretic phenomena then you can use Phoresis effectively and be able to model it accurately.

So that your end result becomes predictable, if it is predictable it is controllable, it is optimise able, so that is why it is very important to understand some of these more subtle effects of how Phoretic forces play a role in affecting your deposition rates in the system. So we have essentially looked at 2 phenomena, the Stefan blowing phenomena and the Phoresis phenomena in which the former does not violate the analogy condition the latter does.

In the next lecture we will take a look at couple more of these homogeneous chemical reactions and heterogeneous chemical reactions and we will take a look at how they can be represented non-dimensionally and we can assess that effect on the prevailing mass transfer rates and processes. Okay, so let us stop at that point, any questions? See you in the next class.