Chemical Engineering Principle of CVD Processes Prof. R. Nagaranjan Department of Chemical Engineering Indian Institute of technology Madras Module-2 Lecture 17 CVD transport phenomena: mass transfer mechanism

Good morning and welcome to our next lecture in our course on chemical engineering principles of CVD process. In the last few lectures we have been discussing the mass transport processes that deliver the depositing material to a substrate and result in the formation of CVD film. We started by discussing certain basic assumptions that you have to make before you define the system and the surroundings.

We talked about how to define various types of control volumes for the problem at hand and then the outline some of the general conservation principles and constitutive relationships which are used to provide closed forms solutions for this conservation laws. In particular, we look at the constitutive laws governing mass diffusion are Fick diffusion being the predominant form of diffusion of mass.

And we also looked at the diffusivity coefficient which is a key parameter that determines the rate at which material defuses in a CVD system and the fact that diffusion coefficient can be estimated either from first principles such as the kinetic theory of gases or by doing experiments and so the fact is that the diffusion coefficient is one that depends very much on the surroundings in which the diffusion species finds itself for example diffusion of trace vapor in a dense gas follows a very different pattern compared to diffusion of an absorbed species on solid surface.

So there are appropriate diffusion rate equations for each situation and they have to be applied properly. Now once we have the ability to calculate diffusion rates the total deposition flux of, for example a CVD film onto a substrate can be calculated on the basis of, as we said in the last lecture 3 components that is conviction, there is diffusion and then there is Phoresis.

Phoresis the first 2 essentially at convective motion but one which is not the same has the convective motion of the host fluid. It is actually conductive that occurs that is separate from the convective motion of the fluid itself. For example when you have an electric field applied across flow feel, the flow may be predominantly taking place along the flow direction;

however certain species that are present in the fluid which respond to this electrical force field will be convicted in the direction which is different from the direction of the fluid that is in flow.

(Refer Slide Time: 3:32)

Therefore the total diffusive flux of the species must be estimated as mi dot double prime which is the mass convective or the mass flux of the i species, again remember that the dot represents per unit time and the double prime represents per unit area, so this is a flux term, so this can be written as mi dot double prime conviction plus mi dot double prime Phoresis plus mi dot double prime diffusion mi and this the diffusive or the convective flux of species i due to the conviction of the host fluid itself can be simply written as m dot double prime conviction times omega i.

In other words just the convective flux of the entire fluid multiplied by the mass fraction of the ith component in the fluid, so this gives you the convective flux of the ith species plus you have the Phoretic flux plus you have the diffusive flux, this again you can write as, this is essentially rho times V where rho is the density of the host fluid and V is the prevailing convertible (()) (5:05), so we can write this as rho V times omega i plus the Phoresis term plus the diffusion term and finally you can write this as rho i times v plus by simply multiplying rho times omega i.

So it is basically the mass density of the ith species in the system times the prevailing convectible (()) (5:33) plus, now this term can be written as rho i times Ci that CI is the characteristic velocity that is induced on the species by the presence of an applied field

whether it is gravimetric field or whether its thermal field or an electrical field or an magnetic field whatever it is, it induces a velocity Ci which we call Phoretic velocity.

Ci is actually the differential velocity from the prevailing mainstream velocity, so it is not an absolute velocity but what we call a drift velocity it is the velocity that represents a differential between the prevailing velocity to the velocity that is induced by the applied field and here we have i subscript because this velocity is going to be unique for every species that is present unlike the convective flow velocity V which is common for all species represent the Phoretic velocity will be different for the different species that are present in the system and of course the diffusive flux as we have seen before can be written as D rho times gradient in omega i that Di is the fit diffusion coefficient.

(Refer Slide Time: 7:15)



So this is the general expression for the deposition flux of any chemical species i in a CVD reactor and as we have seen before you can write the entire conservation equation terms of del rho i by del t plus divergence of mi dot double prime equals ri dot double prime this is the mass conservation equation for species i where this represents the accumulation term, this represents the divergence term and this represents the reaction term.

What we have done here compared to the way we wrote this earlier, is that we brought the diffusive flux also here. So this mi dot double prime now includes both the convective contributions as well as the diffusive contribution. So you can expand this mi dot double prime as these 3 terms and then if you want you can take the diffusive term to the right-hand side of the equation, okay.

So this is the general conservation Law that you must satisfy to obtain the species mass fluxes but remember that this is not an isolated equation it is coupled to the energy conservation equation and the momentum conservation equation and they must all be solved simultaneously.

(Refer Slide Time: 8:42)



And also recall that once we have evaluated the deposition fluxes of the ith species we also have to evaluate mk dot double prime which is summation over iE of omega ki mi dot double prime where this k represents the keth element and omega ki represents the mass fraction of the keth element in the ith species this really is the critical flux that you are after because in a CVD reactor the element that is depositing is present in many many species.

So there may be you know 100 species that contains silicon which is the CVD film we are trying to achieve but in order to attain the actual deposition flux or deposition rate of silicon you have to do this weighted summary of the deposition fluxes of all species containing silicon and you have to verify that this is greater than 0 in order for the deposition process to happen.

(Refer Slide Time: 9:55)



So for example if silicon is going to be your depositing film than the mass flux of silicon has to be positive when it is equal to 0 we call that the dew point, when it is positive deposition is happening when it is negative what that means is, a pre-existing film on the substrate may actually start evaporating.

(Refer Slide Time: 10:19)



And also recall that when your CVD film has let say to species that are present for example if you are trying to make W-Si composite then you really need 3 constraints, so m dot Si has to be equal to 0, m dot double prime of W has to be is greater than 0 and as a third condition your m dot double prime silicon divided by m dot double prime tungsten must be in the stoichiometric ratio.

If it is going to be a Si3W4 film then the molar fluxes not the mass fluxes you have to convert these 2 molar fluxes, the molar flux have silicon to tungsten must be in the same ratio as the stoichiometry that prevails in the condensate. So it is important to keep checking for self consistency when you run the transport model for the CVD reactor and you try to estimate your rates of chemical vapor deposition.

(Refer Slide Time: 11:30)



Okay, before we proceed further let us take closer look at this parameter Ci because it is going to be important to know how to calculate this Phoretic velocity under various prevailing fields.

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In general Ci is defined as a prevailing force a body force divided by a friction coefficient fi or it can also the denominator can be looked at as a friction coefficient or as the inverse of mobility coefficient for example let say that gravity is the field that is being applied on top of the convective field that is present in the system. Now gravity is typically a negligible effect for very very small molecules. However in certain CVD reactors you do use larger molecules where gravitational settling can actually become important, once molecules get to be so big that they are of the same size as small particles then gravity does become an important effect.

 $\begin{aligned}
 C_{i} &= \frac{P_{i} J_{i}}{J_{i}} \quad finction \quad coef \\
 finction \quad coef \\
 (mobility)^{-1} \\
 J_{i} &= gravit, \\
 J_{i} &= gravit, \\
 f_{i} &= STT \quad disetf \quad p \\
 C_{i} &= C_{i,s}
\end{aligned}$

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So in that case when we talk about gravity settling or sedimentation, gi will now become the acceleration due to gravity in general gi can be any body force or body acceleration but in the case of gravitational settling gi will be equal to gravity and fi will be equal to 3pi times the effective diameter of the species times mui and correspondingly the Ci value that you calculate be the sedimentation velocity or settling velocity.

So if you have a CVD reactor in which in addition to convection and diffusion, if we know that the vapors that are present are large enough to be considered very large molecules or small particles then you have to consider the gravitational force as a field which can influence the motion of these large molecules. (Refer Slide Time: 14:18)



Now similarly, in the case of let say you have an electrophoretic field, the numerator rho igi will now be the corresponding force that is exerted on the vapor due to the electrical field or electrophoretic field that is present in the system and the value of Ci that you will calculate will be the electrophoretic velocity of species i, if you have thermal field Ci will be CiT will be the Thermophoretic velocity.

In this particular case the force the thermophoretic course is proportional to the logarithm of 1 over T and the force field itself we will talk about it in little more detail because thermophoresis or thermal diffusion is a very important parameter in CVD systems particularly in cold wall systems because the temperature gradient between the substrate and the reactor walls can be quite large in such CVD systems and thermal diffusion which is the diffusional motion of vapours due to temperature gradient can become an important effect, so we will spend a little more time later in the course talking about how to estimate the thermophoretic diffusivity.

So in general this Phoretic fields can be comparable in magnitude to the convection feel that is present as well as the diffusion field that is present. How do you assess when Phoretic feel is important or not? So here again let us take gravitational or initial fields as an example, so I am sure you all have heard about stokes number. (Refer Slide Time: 16:24)



The stokes number is a reflection of the inertial characteristic of the settling material, right? Now I think you have probably studied stokes number in the context of particles but many of the same conclusions also apply in the case of heavy molecules which are encountered in CVD reactors and which behave like small particles. So stokes number in general can be defined as a characteristic particles stopping time and a characteristic flow time where the flow time is simply a characteristic dimension in the system divided by characteristic velocity in the system, tp is the time take for the velocity of the particle to drop by a factor of 1 over E, right?

Now in the case of again gravitational settling this value can be calculated once you know the density of the species and its characteristic size, so if you recall the stokes number expression basically looks like this the numerator is rho idi squared over 18mui and the denominator is 1 over u.

(Refer Slide Time: 18:08)



Now when this number is much smaller than 1, this implies that essentially inertial effects are absent whereas once this approach is about 0.1 or larger in inertia it is important to consider. Now what we mean by inertia in the case of CVD reactor, again inertia is hugely associated with particles and the conventional view of inertia is if you have particles that are entrained in a fluid and the fluid approaches the surface, the fluid tends to flow essentially along the surface.

Whereas the particles deviate from the streamlines of flow and actually impact the surface, right? Because of the inertia that they have, so the higher the inertia that the particles have the greater will be the velocity with which they strike the surface. Now in the case of heavy molecules or vapours they can also possess sufficient inertia to deviate from the carrier gas flow streamlines as they approach a surface such as a substrate on which you are trying to produce a CVD film.

Now inertia flows are especially important when we use stagnation flow consecration for a CVD reactor. If you recall essentially there are 2 predominant types of CVD reactors, one in which the flow approaches the way for an horizontal direction and one in which the flow approaches the way for in the vertical direction and in the latter case the inertial effects associated with large vapor molecules can become significant and result in mostly an enrichment of deposition at in the stagnation region.

And so it is important to be able to calculate this ratio and verify whether it is much smaller than one. Now in the case of heavy molecule if we calculate the stokes number and find that inertia is negligible than you can essentially also ignore the Phoretic affect due to gravitation then you calculate the total deposition flux. If on the other hand when you calculate the stokes number you find that it's a value that is comparable to 0.1 or higher than you cannot neglect the inertial flux of deposition and so you have to take inertial deposition also as a mechanism that brings material to the substrate.

(Refer Slide Time: 21:30)



Now in the case of turbulent flow which sometimes happens in CVD reactor despite our best efforts to avoid it the t flow instead of being simply defined as characteristic length divided by characteristic velocity in the case of a turbulent flow t flow is defined as a characteristic length scale for the turbulence divided by a u prime u prime to the power half where these are the RMS root mean square velocity's that are associated with the turbulent field.

So t flow in the case of laminar flows this is defined as L by U but in the case of turbulent flow you have to calculate essentially t flow for turbulent flow which reflects the fluctuations in the flow field. Now another view of t flow in the case of turbulence is based on the view of eddy diffusion you know where you view turbulence is essentially transport of materials by the flow of large eddies that are present in the flow field.

(Refer Slide Time: 22:47)



And in this case you can write the flow field or the characteristic time in the turbulent flow field as over Epsilon kt that kt is the turbulence kinetic energy per unit volume of fluid and Epsilon is the turbulent viscous dissipation per unit volume of fluid, have you heard of the kt Epsilon model of turbulence?

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Most of the cft codes essentially use kt Epsilon as the parameter to model a turbulent flow feel and you can essentially relate that back to stokes number by looking at it this way that the characteristic flow time in the case of turbulent flow field which is characterized in terms of eddy propagation and written as t flow equals t eddy which is equal to Kt over Epsilon and Kt is the turbulence kinetic energy that is contained per unit volume of fluid divided by Epsilon which is the turbulent viscous dissipation per unit volume of fluid.

So your numerator in either case remains the same, so tp or goes in the case of CVD this is t of HM which is a heavy molecule remains the same whether or not it is a turbulent flow field or a laminar flow field what changes is just the denominator. So when you are trying to calculate the stokes number in a CVD reactor the first thing you have to verify is you in a laminar flow situation or in a turbulent flow situation depending on whether the prevailing flow is laminar or turbulent you have to use the appropriate value for the denominator t flow and then you calculate the corresponding stokes number and then you verify whether it is much smaller than 1 or starts approaching 0.1And then you apply the correction factor to the total deposition flux.

So in terms of calculating total deposition flux, again remember there are 3 components, one is simply associated with a convective flow of the carrier fluid, the second is associated with the Phoretic motion of the species in the presence of an applied field and the third is diffusive flux. Now once you have calculated all these fluxes, you know as chemical engineers we always like to use non-dimensional terms, right? So we have to define such a non-dimensional parameters to characterize deposition fluxes happening in a CVD reactor.

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Professor: Now there are 2 non-dimensional parameters that are conventionally used to represent mass fluxes, mass transport, do you know what they are? 2 numbers, Schmidt number and...

Students: (()) (26:01)

Professor: (()) (26:04) and Schmidt are, okay. Sherwood number, what situation does that apply for? Can you use that number? Sherwood number is simply ratio between new and the I mean it does not really tell you anything about the flux of mass but any other number that you are aware of?

Schmidt number and Lewis number simply are ratios of diffusivities, when you actually talk about fluxes of material or rates of transport the Sherwood number is 1, the Sherwood number is also known as the Nusselt number. I think in the US they call it Nusselt number elsewhere they call it Sherwood number but there is a second one Stanton number, okay.

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Nusselt number and Stanton number are the 2 critical dimensionless parameters, so how do they differ, when do you use which one? When to use the Nusselt or Sherwood number, is there a particular flow situation where it is most appropriate? See it depends on what you use as your reference flux, so I mean in both cases what you do is, you take the prevailing diffusive flux and you divide it by reference Max flux and by the way this is also the same both. So obviously what is different between the 2 is your denominator, what you use as your reference mass flux.

Now in the case of the Nusselt number the reference mass flux refers to a diffusive flux I mean a flux that is given by a concentration eddy whereas in the case of a Stanton number you use a convective flux as your reference flux, so basically the Nusselt number or Sherwood number is appropriate then you have either a static situation, a stagnal flow situation or a very low velocity flow situation, very low Reynolds numbers.

Whereas the Stanton number is typically used when you have large convective velocities that are present.

(Refer Slide Time: 29:03)



So in the reference mass flux, in the case of the Stanton number is simply rho times U times omega i W minus omega ie where W and e refer to if this is your substrate on which the CVD film is forming this is typically referred to as station W, it is the point at which the deposition is happening and e is outside of the boundary layer, so it is called the free stream layer or the mainstream layer.

(Refer Slide Time: 29:24)



So it is at a point that is sufficiently far away from the substrate that this velocity is essentially a uniform velocity, so the prevailing velocity at this point e will be the same as the approach velocity or the entrance velocity of the fluid. Of course the velocity will drop to 0 at

the substrate. So omega iw basically refers to the mass fraction of the ith species at station W in your system and Omega ie refers to the mass fraction of the ith species far away from the substrate.

(Refer Slide Time: 30:38)



How about reference mass flux for the diffusive case, how would you similarly write it? It should be some omega iw minus omega ie divided by L, right? Times, so it is the actually, the mass fraction gradient that is present across the boundary layer which leads to a diffusive effect.

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Let us take the units here, this is kilograms per meter cube times meters per second, so this has units of kilo grams per meter squared second bit is the unit of flux. How about here this has units of one over meter.

"Professor -Student conversation starts"

Professor: What is the unit of diffusivity?

Student: Meter square per second.

Professor: So this currently has units of meter per second. So I have to multiply this by rho, right? Which is kilograms per meter cube which will give kilograms per meter square seconds.

"Professor-Student conversation ends"

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So the units or the reference mass flux in the case of Nusselt number is rho Di times omega i W minus omega i by L and the reference mass flux for the Stanton number is rho u times omega iW minus omega e and what is in the numerator?

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It is a prevailing diffusive flux, so that is what we have been calling ji w dot double prime or you can write it as rate divided by an area, so you can also write this as jiw dot divided by Aw where jiw dot is the mass deposition rate that is mass arriving per unit time divided by the area of the substrate Aw. So it is just different way of representing flux as a rate divided by an

area and as we said the same numerator will apply in the latter case also in the case of Stanton number.

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There is one more important non-dimensional parameter and that is called capture efficiency. Capture efficiency is defined as total rate deposition onto a substrate divided by the total rate at which mass is flowing pass the substrate and it is denoted by a symbol eta cap. So in terms of deposition rates how would you now define this? The total deposition rate, you take the total deposition flux and multiply it by the area.

So we have previously calculated minus mi dot double prime by taking into account the convective contribution the Phoretic contribution, the diffusive contribution and so on. Take this value and multiply it by Aw which is the total area of the substrate and that gives you the total deposition rate of species i onto the substrate.

Now you multiply this by rho times U times omega i in the mainstream omega ie times Aw projected which is the project surface area of the substrate. In other words the area over which the fluid will be flowing. So the denominator here rho times U times omega ie times Aw projected gives you the total rate at which mass is flowing across the substrate and the numerator gives you the rate at which is actually depositing at the substrate.

So in other words if the substrate was essentially catching all the material that flows past it the capture efficiency will be 1, right? So essentially the higher the capture efficiency the more efficient your CVD system is, something you want to maximize, your eta capture should be as close to 1 as possible in a CVD reactor in which you are trying to make a CVD film.

Now we also talked about some other CVD cases where you are actually trying to prevent a position. In such cases you should try to design the system so that the capture efficiency is as close to 0 as possible. So depending on the application at hand this is an important parameter to try and optimise by tweaking it. Now how are these related? I mean is there a way to relate the capture efficiency for example to the Stanton number? You really cannot relate it to the Nusselt number because the denominator is different in the 2 cases.

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However if you look at the Stanton number and the capture efficiency you will see that, essentially the denominators are the same except that you know you have this projected area also in the denominator. So if you take the ratio for example of and the number to the capture efficiency and let us say that, let us make some assumptions for example that omega iw is very very small compared to omega ie, so that the omega ie will cancel out then this ratio and also assume that you are deposition is dominated by diffusion.

Assume that the contribution due to convection and Phoresis is much smaller compared to the contribution due to diffusion, again that is a good assumption in a CVD reactor because primarily you are trying to achieve film formation by diffusion process rather than a convective process, printing on the other hand is a convective deposition process but CVD I design you more to make a diffusion dominating.

(Refer Slide Time: 37:57)



So in general you can see that it is true that diffusive deposition will dominate over convective and Phoretic deposition in a well-designed CVD reactor. So given that if you assume that jiw dot is equal to miw dot and you assume that the diffusion is so efficient that material that is present the substrate is virtually 0. In other words as soon as the material comes to the substrate it is forming a film then you can actually relate these 2 and they will be related by St over the capture efficiency will be equal to Aw over Aw projected, is that correct?

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No actually it should be other we around thus eta capture is in the denominator and the capture efficiency, so it should be, so what does that mean? When you look at this ratio of projected area to total area it is always less than 1, right? And in fact in most flow situations particularly in a CVD reactor it is half or less than half because you know only one side of the substrate is really being exposed to the deposition.

So this number is roughly less or equal to 0.5, so you can see that the Stanton number is roughly half of the capture efficiency or another way of stating it is, if you know the Stanton number for the system you can actually calculate the capture efficiency as, once you know this ratio what is the ratio of the projected area to the total available area? You can actually start relating to some of these dimensionless parameters.

So that is the value of representing your system in terms of dimensionless numbers. You can start interpolating and extrapolating beyond what you actually calculate or what you actually measuring your system. So when you talk about mass transfer in CVD reactors, again that the 3 most important dimensionless numbers that you have to remember are the Nusselt number again which applies in the case of laminar flows, low velocity flows, stagnant flow conditions, Stanton number which primarily applies in convective flow conditions and the capture efficiency which relates how effectively the substrate is able to scavenge the depositing material from the gas phase and incorporated into a CVD film on the surface.

Once you have calculated these dimensionless numbers from the viewpoint of modelling or simulating a CVD system the key thing that you have to start characterizing next is, how does

this Nusselt number change? For example as a function of time or as a function of spatial location. You have to start mapping your Nusselt numbers because these are local values, right?

And so you can actually do a three-dimensional analysis of how your dimensionless numbers vary inside a CVD reactor and you try to optimise design of the CVD reactor in order to achieve a certain distribution of this dimensionless numbers. For example if you have a stagnation flow reactor then the most appropriate numbers for you to use the Nusselt number and the capture efficiency.

The Nusselt number is simply a reflection of how efficiently material is being delivered to the surface. Capture efficiency is the representation of how effectively that material is being converted to a film that is sitting on top of the surface. So you really have to keep your eye on both the parameters when you have to try and optimise both parameters and the methods you use will be very different.

For example if you are trying to increase your Nusselt number is typically you will do that by using, for example lighter species because lighter species will diffuse faster, so the diffusive flux will be enhanced or you will do it by reducing pressure or by increasing the pressure, right, these are very common methods that are used to increase the Nusselt number and if you are trying to increase the Stanton number the primary variable you have is the velocity.

As you increase the convective velocity your Stanton number will also tend to increase in the system because it is convection dominated. However if you are actually trying to maximize the rate at which the film grows on the surface then you shall also be simultaneously maximising your capture efficiency. The capture efficiency is more a reflection of the addition or the accommodation of the arriving molecule by the surface of the substrate.

So that depends on parameters such as surface energy, so if you have a surface that has high surface energy is it is more likely to retain the arriving molecule compared to a low energy surface. So one of the few would want to do for example if you are trying to put down a CVD film on Polymer which has a very low surface energy the first thing you will do is treat the Polymer with plasma for some means in order to increase its surface energy.

Because the high surface energy has an immediate effect on the capture efficiency. He would also want to maximize your and molecular addition parameters such as the (()) (44:06)

constant. The (()) (44:07) constant is a reflection of Van der waals force that prevails between 2 adjacent molecules and again the higher the (()) (44:16) constant or the higher the Van der waals forces of addition the higher will be the value of your capture efficiency.

Even surface topography can play a role, for example if you have a rough surface its ability to capture mass is very different from a smooth surface. In general a rough surface gives you more surface area and therefore potentially there is more room for material to deposit. However the downside of that is, on a rough surface the CVD film is not going to have a smooth and uniform topography.

So that is the downside, so you can increase the amount of material that condenses by roughening the surface but you lose some control over how well and how uniformly the film is deposited on the surface but in any case the key thing to remember is that these are 2 distinct parameters the Nusselt number and Stanton number dictate how material is delivered to the surface.

The capture efficiency dictates how that material is accommodated and used to build a film on the surface and so the 2 have to be taken separately and if you are interested in optimising or maximising your CVD rate then you have to separately maximize both of these and you also have to look at how the 2 or in synergy the sometimes a higher mass flux to the surface can actually result in a lower capture efficiency.

So it also depends on the capacity of the surface to accommodate the arriving molecules. All of this has to be taken together in order to fully optimise the system for achieving the CVD rates and film growth rates that you are looking for. Okay, so we will stop at this point, they have been making some very implicit assumptions here particularly about what you call the mass transfer analogy condition.

So in the next class or to we will look at situations where this mass transfer analogy breaks down and what affect that has in our calculation of deposition fluxes. Okay, any questions on what we have covered today? Okay, so I will see you can the next class then.