Chemical Engineering Principle of CVD Processes

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Module-2

Lecture 16

CVD Transport Phenomena: Constitutive Laws

Good morning and welcome to the next lecture in our course on chemical engineering principles of CVD process. In the last lecture we started covering the basics of transport processes that occur in CVD systems and we started out by classifying various types of chemically reactive flow systems in terms of the basic characteristics discussed how to define volumes for various applications and then we discuss the conservation laws governing mass conservation, momentum conservation, energy conservation and entropy conservation.

Towards the end of the lecture I mentioned that the right-hand side of the conservation balances reflect the constitutive equations that are needed to close the system of equations, constitutive laws actually the name itself constitutional means that it depends on the Constitution of the system or the fluid. So constitutive law by definition unlike conservation laws is specific to the system or fluid under concentration.

It is necessary to provide closure to the conservation equations, the 3 most predominant types of constitutive laws or the equation of states chemical kinetic equations and rate expressions and diffusive fluxes and when we talk about diffusive fluxes in particular parameters such as viscosity, thermal conductivity and diffusivity become important now in general a diffusive. Now in general a diffusive flux law can be stated in a linear fashion you can say that the flux is proportional to the prevailing gradient of the field the density parameter that is relevant.

So for example the mass transfer diffusive flux can be taken to be linearly proportional to the prevailing concentration gradient. The heat flux can be taken to be proportional, linearly proportional to the prevailing temperature gradient and so on. Now this linearity is a critical assumption because it implies several things. Most importantly it says that the flux that is happening, diffusive flux that is happening at any location at any instant in time is independent of the events that are occurring far away from that location and events that occurred for back in time.

So as we were discussing yesterday action at a distance affect and also the memory effect or presumed to be absent when you define diffusive flux loss and that greatly simplifies how a definition of the diffusive flux law. Now if we take momentum diffusion as we mentioned yesterday, momentum diffusion is reflected as a stress term.

And in particular the pie operator which has the 2 components the thermodynamic pressure component and the extra stress or viscous stress component is a reflection of how momentum defuses.

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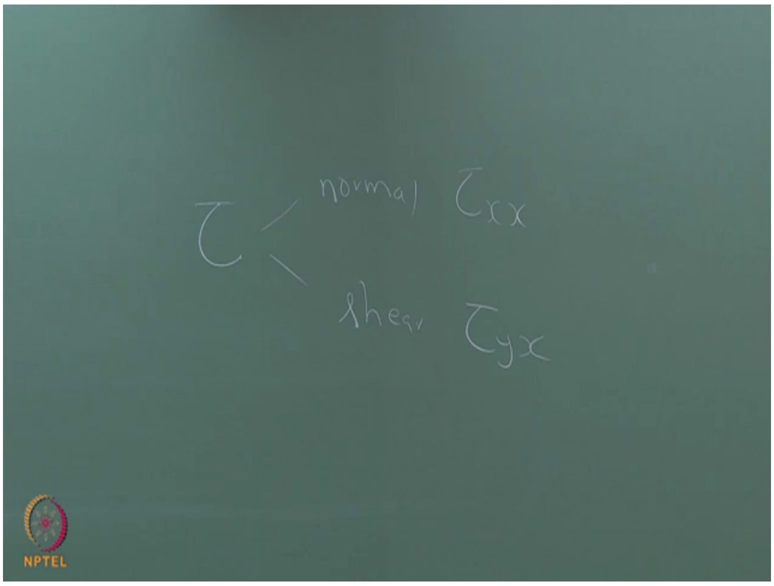

And if you look at the second component Tau which is the stress term, as you know that there is 2 types of stresses, there is a normal stress and the shear stress. Normal stress is typically expressed as some Tau xx and the shear stress would be expressed as Tau yx. Shear stress by definition is the action of a force in a direction x which is acting on y directional force acting on a surface in the x direction, right?

As you will see when you have flow past of flat it and things like that and you know that this Tau yx term is related to mui times Del Dx by del y where this mui is called the viscosity coefficient and of course new is different for different fluids every gas has a different viscosity, every liquid has a different viscosity and so on. Now in order to then close the momentum conservation equation and need to know what is the Tao term in order to know that you need to know what is mui?

And how do you estimate mui, there is basically 2 ways mui can be derived from the kinetic theory of gases, you know, from first principles or it can be experimentally determined essentially you run shear stress for example as a function of various velocity gradients and take the slope and that will give the viscosity coefficient. So in constitutive laws the constitutive coefficients can be derived either theoretically from first principles or phenomena logically from observations of experiments.

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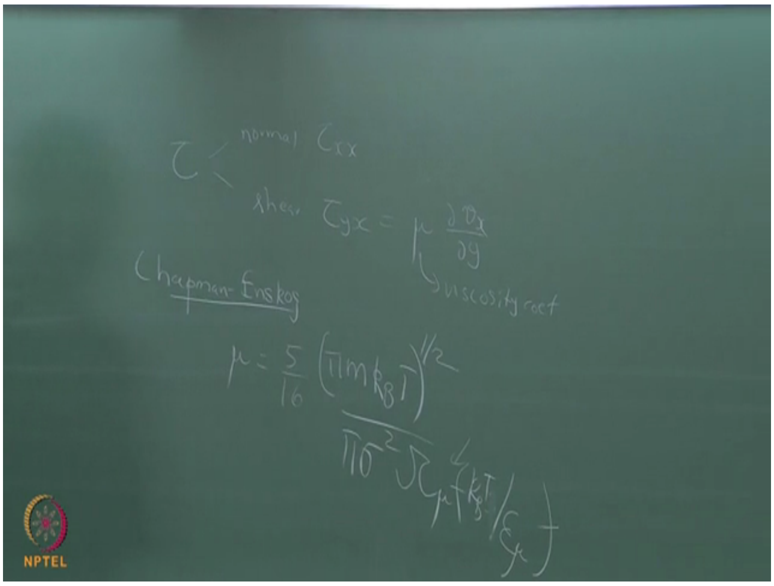

I am sure you are familiar with Chapman Enskog, have you read that in your fluid mechanics? Chapman Enskog, which says that for viscosity particularly of low-density gas mui can be related to the other properties by the following equation pi mkBT to the power half over pi Sigma squared omega mui which is a function of kTB over Epsilon mui, have you seen this expression, does it look familiar?

So it is basically a way of relating viscosity to the molecular weight of the species of the liquid or the fluid, the Boltzmann constant the prevailing temperature, Sigma is the molecular size or it is the spacing you could say between adjacent molecules and this parameter is actually a correction factor for the fact that not all molecules behave like hot spheres, so it has all the hot spheres correction. And this depends on this parameter kT, sorry it is kBT not kTB Boltzmann constant times temperature.

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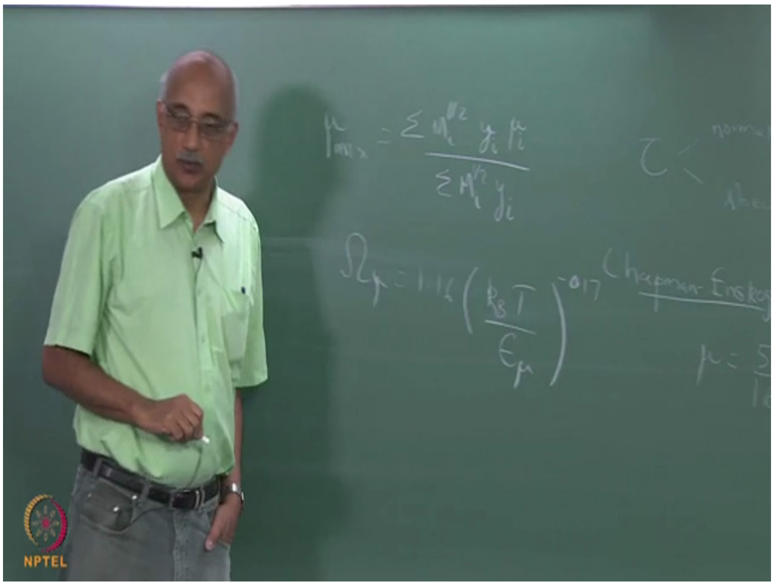

So the 6 omega mui can be written as some 1.16 times kBT by Epsilon mui to the power minus 0.17 I think where this Epsilon mui is basically an activation energy barrier for fluidity of the fluid. So this is the general expression governing the dynamics viscosity of the fluid. If you have a measure of fluids you can estimate the mixture viscosity as summation of mi to the power half yi mui i divided by summation mi to the power half yi are again m’s the molecule weights and y sort the mole fractions.

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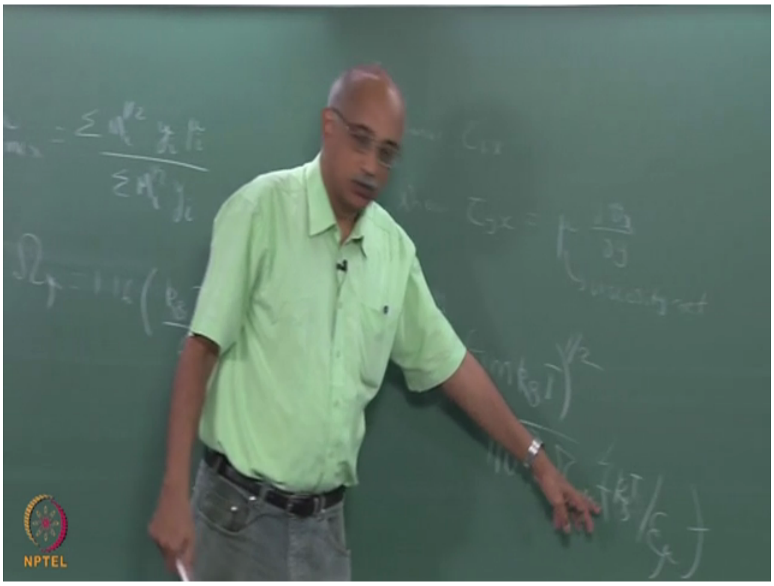

If you look at the temperature dependence of mui, you can see that for a gas the temperature dependence is fairly weak is about 1.5 to 1.8 because according to this you have T to the power half dependence but there is also temperature dependence that is built-in here and so the net effect is fairly a weak dependence of mui on temperature. Of course for liquid you know the viscosity has a significant dependence on temperature. As the temperature increases the viscosity will decrease and again that depend on the activation energy or fluidity of the fluid?

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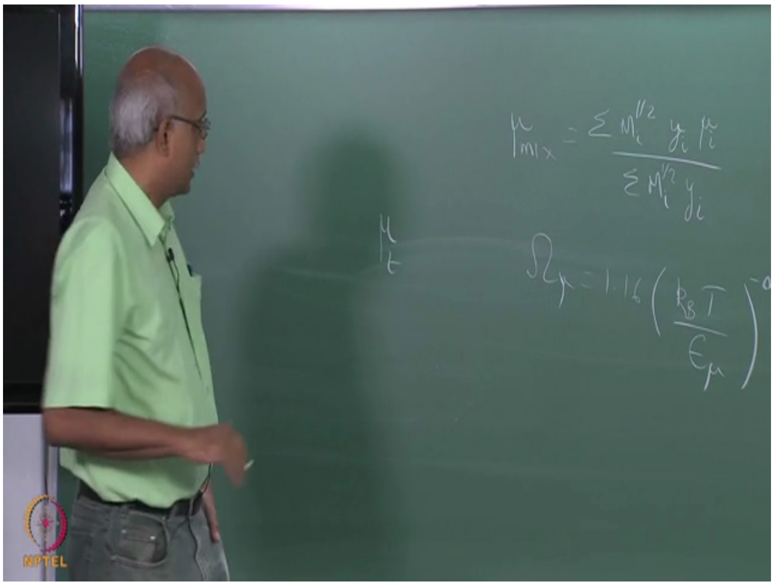

When you have turbulence in the system restore villain viscosity mui t that is introduced and mui t plus mui is the mui effective which is the prevailing viscosity of a turbulent fluid is essentially the sum of its viscosity and the laminar conditions plus a turbulence induced viscosity of the fluid.

So the net viscosity can be written as mui effective equals, mui plus mui t. So that is just a very quick recap of how the dynamic viscosity of a fluid can be calculated essentially from the kinetic theory of the gases.

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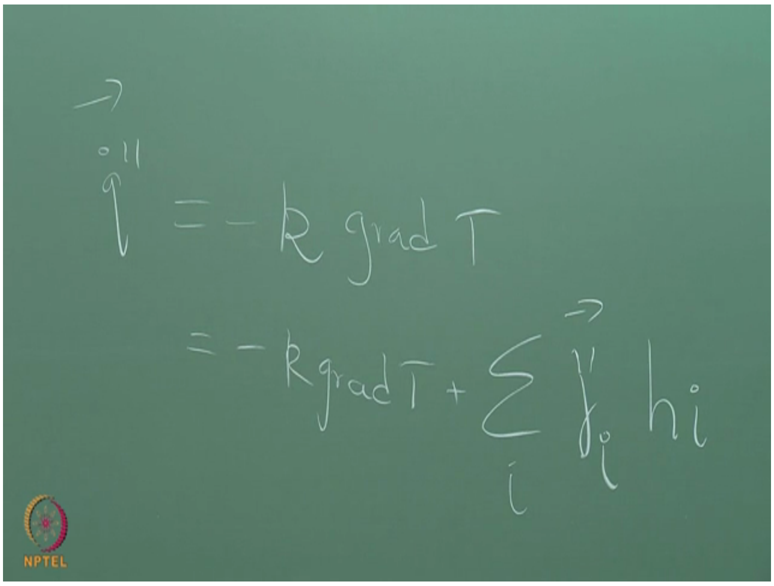

$$\vec{\dot{q}}'' = -k \,\mathrm{grad}\, T$$
$$= -k\,\mathrm{grad}\,T + \sum_i \vec{\dot{j}}_i'' h_i$$

Now when we look at heat flux you know that there is Fourier heat flux law which says that Q double prime equals minus k gradient in temperature where k of course is the thermal conductivity. However this is for essentially a situation not involving mass transfer, as I mentioned yesterday when you have heat fluxes in systems that involve multi-component mass transport, you need to include another terms summation over i ji dot double prime hi which accounts for the fact that as species diffuse enthalpy also defuses and that set up a heat flux as well. So in general expression for heat flux in a multi-component chemically reacting flow system such as a CVD reactor as to have a mass diffusion flux related term also built into it.

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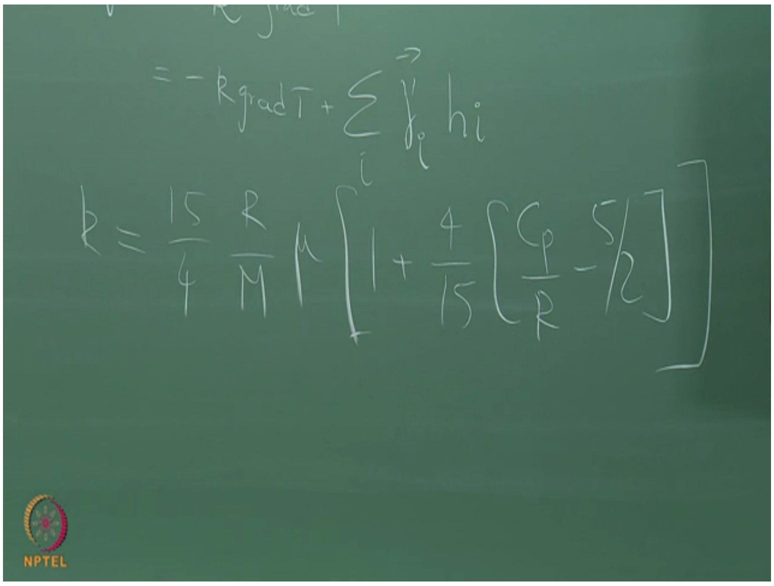

$$= -k \,\mathrm{grad}\, T + \sum_i \vec{j}_i h_i$$

$$k = \frac{15}{4}\frac{R}{M}\mu\left[1 + \frac{4}{15}\left(\frac{C_p}{R} - 5/2\right)\right]$$

Here obviously the key parameter is your thermal conductivity k and again the Chapman Enskog theory says once you know that what viscosity is you can calculate k based on the viscosity of the fluid and the formula for that is 15 by 4 times R by M times mui times 1 plus 4 by 15 times CP by R minus 5 by 2 where CP of course is the heat capacity under at constant pressure.

And k makes a summation over i, in this case it is mi the power 1 3rd yi ki divided by summation over i, mi to the power 1 3rd yi. So thermal conductivity as well it can be measured from experimental observations because thermal conductivity is fairly easy to measure simply by measuring temperature gradients which is much easier to measure comparative velocity gradients obviously.

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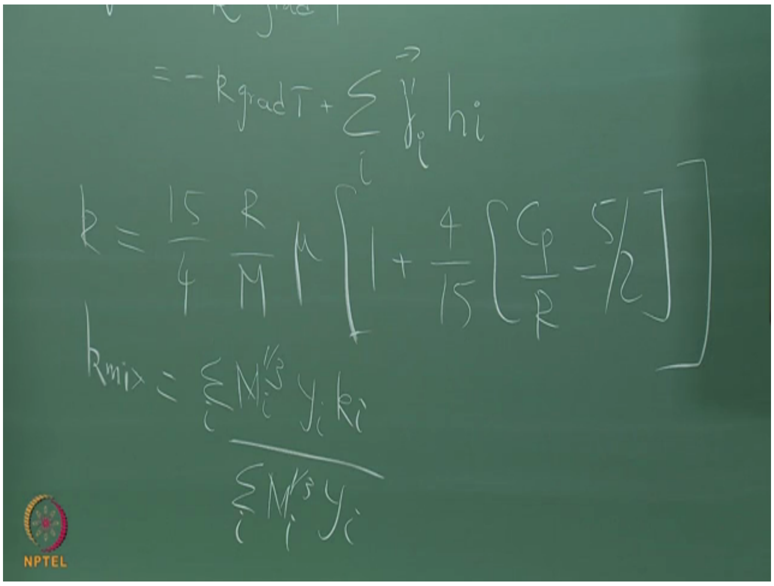

$$= -k \, \mathrm{grad}\, T + \sum_i \vec{j}_i h_i$$

$$k = \frac{15}{4}\frac{R}{M}\mu\left[1 + \frac{4}{15}\left[\frac{C_p}{R} - 5/2\right]\right]$$

$$k_{mix} = \frac{\sum_i M_i^{1/3} y_i k_i}{\sum_i M_i^{1/3} y_i}$$

So thermal conductivity is much easier to measure experimentally, so typically the route that one would take is that if you do not want to calculate mui and k from first principles then you would run experiments to measure k and then use this formula, now that you know k you can go back and there estimate mui, right? Because I said mui viscosity is very very difficult to determine through excellent observations where thermal conductivity can be obtained much more easily.

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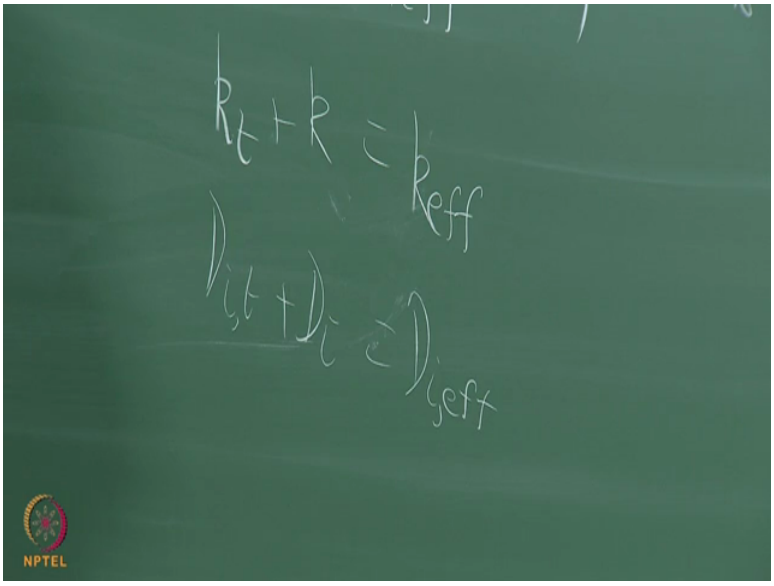

$k_t + k = k_{eff}$

$D_{i,t} + D_i = D_{i,eff}$

And just like with viscosity there is also kt parameter which is the thermal conductivity associated with turbulence plus k will give you k effective and by the way the turbulence terms mui t mKT and we will see later on that similarly for diffusivity there is Dit plus Di which is equal to Di affective where Di the Fick diffusivity under laminar conditions and Dit is the turbulence enhanced Fick diffusivity.

The interesting thing to note is that Dit is absolutely no relation to Di, similarly kT is no relation to k mui t has no relation to mui they are completely independent of each other, mui t, kt and Dit only depends on the prevailing condition and also interestingly mui t, kt and Dit are very close to each other in terms of the relevant ratios.

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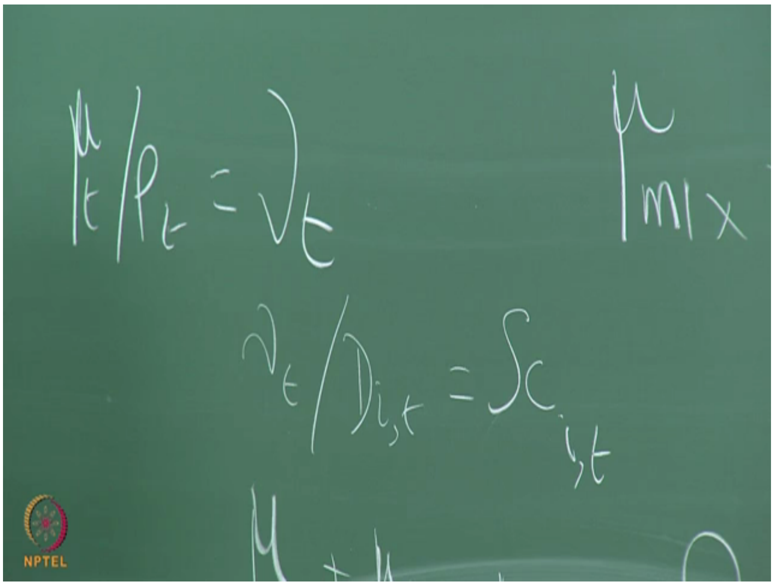

So if you take mui t by rho t which is of course the kinematic viscosity mui t, you know, if you take the dynamic viscosity and divide by density you get the kinetic viscosity. If you take the ratio of mui t to Dit, what do we call that mui by D, any idea? It has got a number, name to it. Kinematic viscosity divided by diffusivity? It is called the Schmidt are Scit.

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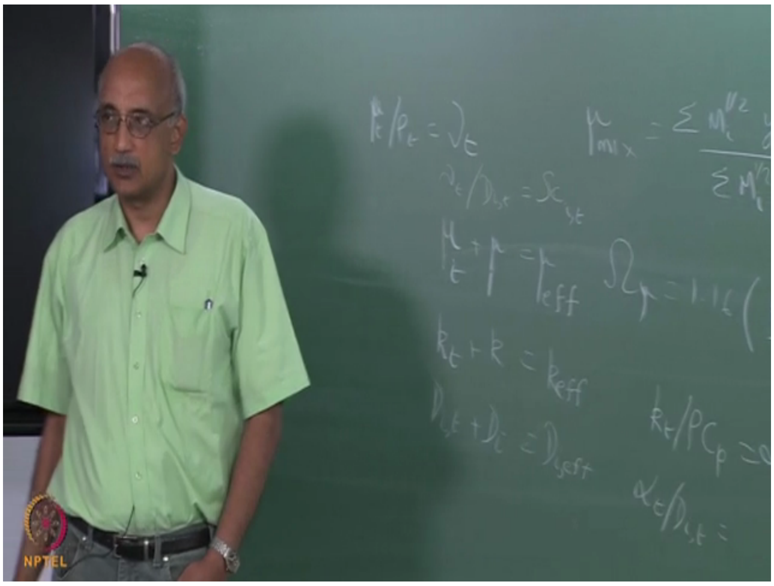

And similarly if you take kT by rho Cp that is called alpha t thermal diffusivity and there is a name for alpha t by Dit, any idea what that is? Lewis number, so the point is all these are actually close to unity. In other words once turbulence sets in the associated kinematic viscosity, thermal diffusivity and Fick diffusivity are all almost equal. In other words once turbulence sets and the affect of turbulence is much more predominant compared to the affect of the fluid itself. So the nature of the fluid does not matter as much as the nature of the turbulence. However under laminar conditions it is a nature of the fluid that really determines this transfer coefficients.

So, let us about diffusivity which is obviously a parameter that is most relevant to this particular course, so we should talk about it in a little more detail. Now according to Fick's diffusion law which he introduced back in 1885, the mass diffusive flux of a species in the case of an isotropic, isothermal fluid is proportional to the prevailing concentration gradient and it occurs in the direction of decreasing concentration, right?

Again these are very important definitions, when we says isentropic what it means is that the diffusivity is equal in every direction and when we say isothermal what we mean is there is no temperature gradient which can also drive mass flux according to phenomena known as thermal diffusion.

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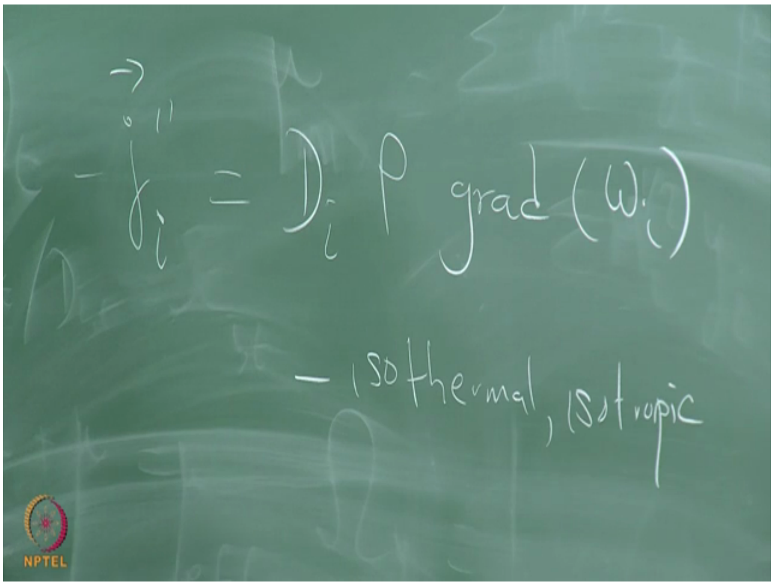

$$-\vec{\dot{j}}_i'' = D_i \rho \, \mathrm{grad}(\omega_i)$$

– isothermal, isotropic

So under these restrictive conditions you can write the diffusive flux minus ji dot double prime is equal to Di rho gradient of omega i as equal to Di rho gradient of omega i again this is for isothermal and isentropic conditions and also there is an assumption here that it is a pure material that is not a mix of species but in the real system particular in the CVD reactor you know that there are going to be hundreds of species.

So the effective diffusion coefficient of a single species is going to be dependent not only on the prevailing temperature and pressure conditions but also the mole fractions of all the species comprising the system because when you have ask a case where you have a dilute species which is diffusing in a low-density gas which is typically the case and a normal CVD reactor.

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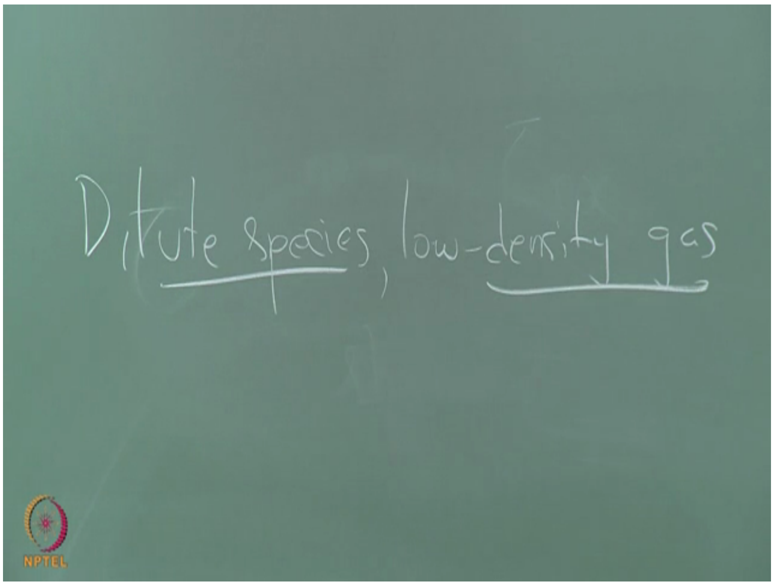

Dilute species, low-density gas

So for that particular combination of a dilute diffusing species in a low-density gas, you can write the effective or prevailing diffusion coefficient as the aggregate of all the binary diffusion coefficients. In other words as these dilute species move around they are going to be encountering other molecules that are present in the system and each binary encounter imposes a certain diffusion coefficient. This diffusion coefficient is basically something that reflects random walk.

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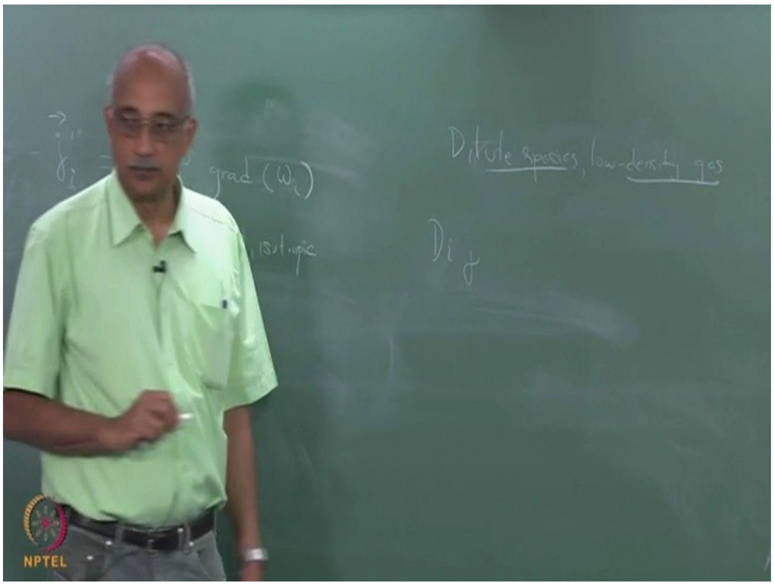

Random walk is basically the distances covered between one collision to the next and so you can essentially estimate binary diffusion coefficient Dij which simply reflects the diffusion a path associated with binary collisions and from this you can estimate that is Di mix the diffusion coefficient of species i in the measure of gases rather than in a binary system.

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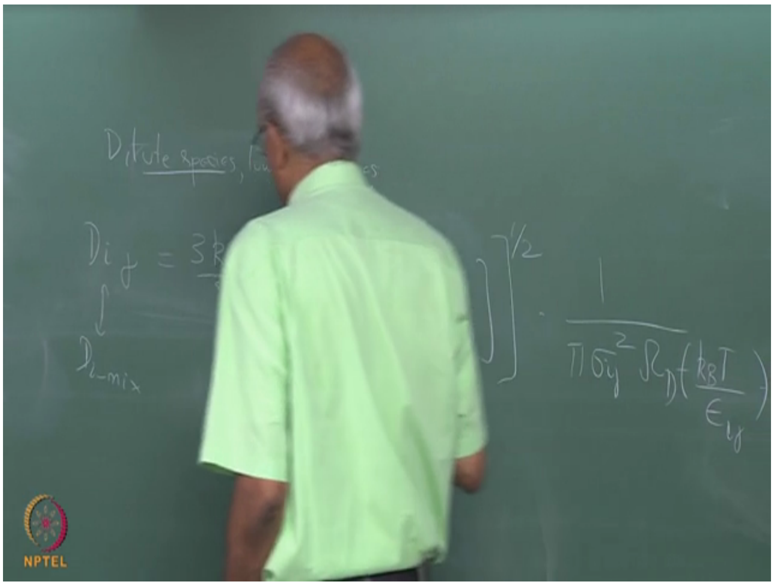

So that is an expression here for Dij which was as 3 times kBT over 8P times pi kBT mi plus mj over mi mj the whole thing to the power half 1 ovre pi sigma ij squared omega d which is a function of kBT over Epsilon d. Okay, so if you compare this expression to what you wrote down for viscosity and thermal conductivity, the key differences are pressure is now a key term and it is the denominator.

As pressure increases diffusivity decreases which is why if you want to enhance diffusion rates you use low pressure system, so that is the important thing to keep in mind. The second thing to keep in mind is here the temperature dependence is close to T times T to the power half or roughly 1.5 again there is some temperature dependence here. So the actual temperature dependence of the diffusion coefficient is roughly T to the power 1.5 to 1.8.

The other thing you need to keep in mind is because we are talking about a binary diffusion process, there is this term called Sigma ij, what that reflects is, the equilibrium distance of separation between 2 molecules.

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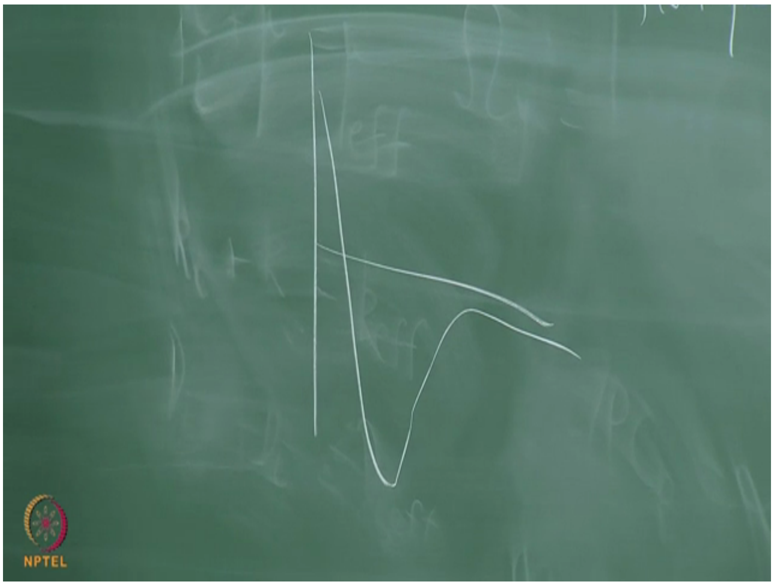

So if you look at the force between any 2 adjacent molecules, Van der waals force for example it will follow this typical pattern where 0 is here and there is a particular distance of separation between the 2 molecules, so what we are plotting here is essentially the Epsilon ij or the intermolecular potential as a function of the distance of separation.

So as the molecules come very close together there is a repulsive force as they move further away there is an attractive force. So there is a particular distance of separation between 2 molecules which results in a net force of 0 which is an equilibrium position of rest between these 2 molecules. So that is essentially obtained by plotting the intermolecular potential between molecules i and j which is Epsilon ij as a function of distance of separation and the distance at which it reaches 0 is what we call sigma ij. So it is intermolecular distance of separation corresponding to the point where Epsilon ij equal to 0.

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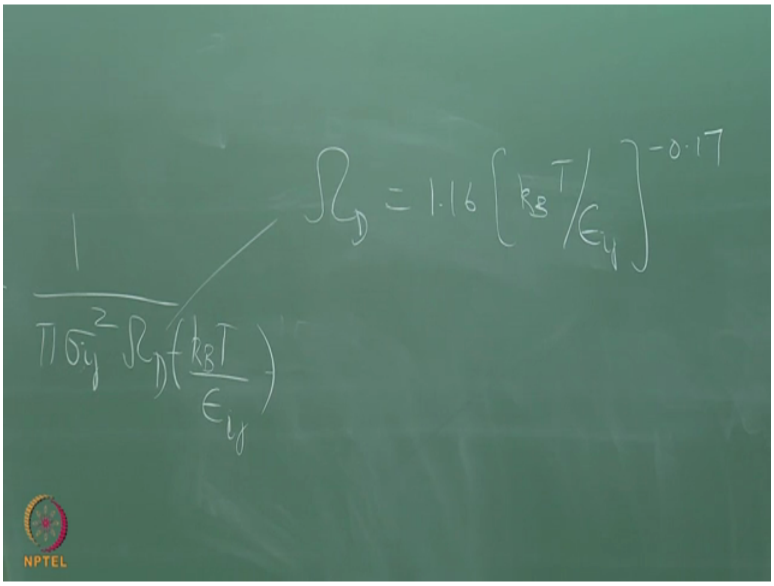

And again this omega D parameter is written as 1.16 times kBT times Epsilon ij to the power minus 1.7 and again it corrects for the fact that the diffusing molecules are not hot spheres. The closer they are to our hot spheres condition the closer omega D will be to 1 but in general you have to include this correction factor. So once you have estimated this parameter the binary diffusion coefficient, the diffusivity of species i in the mixture of species can be derived as 1 minus yi times summation of j equal to 1 to N where j is not equal to i of yj over Dij the whole thing to the power minus 1.

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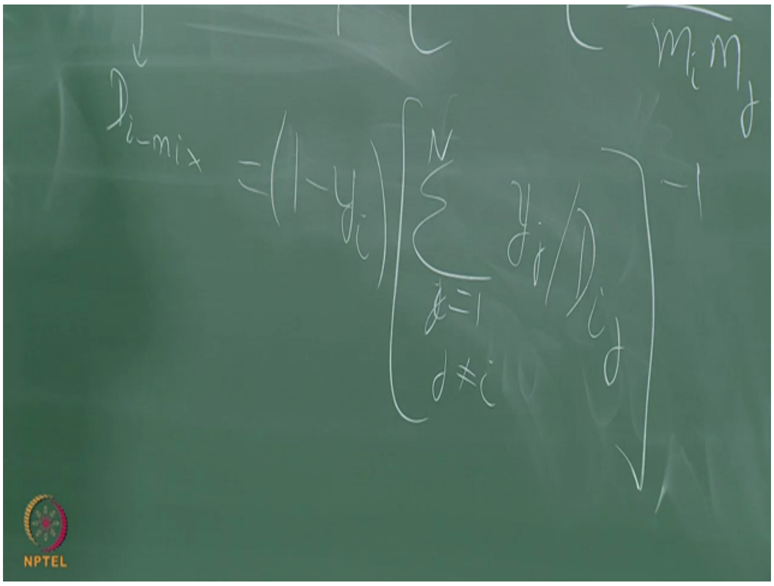

$$D_{i-mix} = (1-y_i)\left[\sum_{\substack{j=1\\ j\neq i}}^{N} y_j/D_{ij}\right]^{-1}$$

So it is essentially estimated as a beaded sum of the binary diffusion coefficients which enables us to calculate the prevailing diffusion coefficient in the case where the collisions are not only binary but multi-species are involved. So once we have estimated the mixture of the diffusivity of species i in the mixture this again we are assuming that it is a single parameter for the system which means you are still assuming isotropic.

The only assumption we have relaxed here is the, you know, the binary assumption we are allowing multiple species to be present and we have estimated the diffusion coefficient in the presence of multiple species but the fact that the only have a single scalar value for Di mix essentially implies that we are still assuming it is an isotropic fluid and that the diffusivity in every direction is the same.

But in reality for many fluids, particularly fluids that are under shear stresses extreme turbulence this may not be a good assumption. So we have to, in such cases realize that what we have defined here is like an effective or average diffusion coefficient which is a scalar representation of the diffusion vector at that is present in the fluid.

Now in the case where you have a heavy species, let say that your molecular weight of the diffusing species exceeds the molecule weight of the carrier gas which can very easily happen in CVD systems because we use H2 as the carrier gas but the depositing species may be SiH4 which is much heavier and larger than the H2 molecule. In such cases how do you estimate the diffusion coefficients?

So here you do not really use a random walk principle to estimate diffusion coefficients instead you go to the Stokes Einstein theory, if you remember which is based upon inertial effects. So you essentially try to track each molecule like particle and you estimate its diffusivity just like you would estimate the diffusivity of a particle in a fluid. So you may recall some of the experiments might have done in mechanical operations and so on to estimate the diffusivity of a particle.

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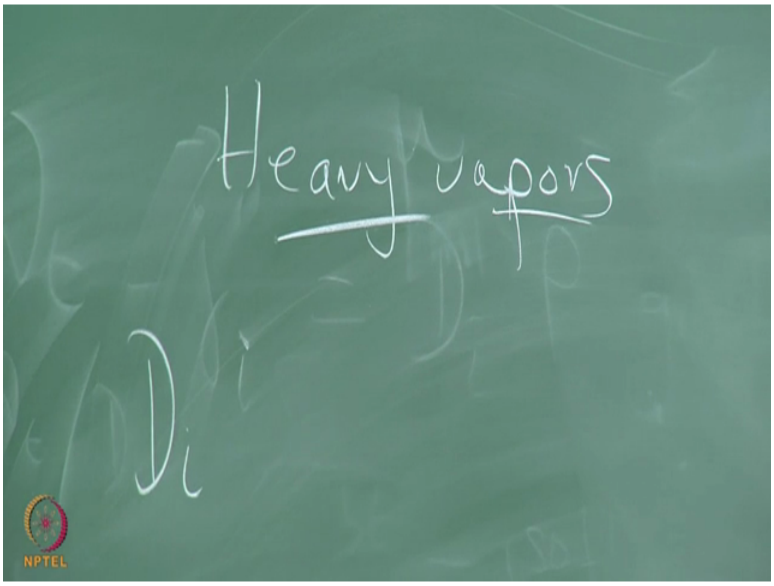

And if you remember the expression that comes out, so this is for heavy vapours in a gas or it could even before solids in a gas or in a liquid. The expression for the diffusion coefficient Di equals kBT over 3pi mui Sigma i effective, right? So in the case of a particle you would simply substitute Sigma with a particle diameter DP but in the case of heavy molecule you use a molecule size the effective molecular size of the species appears in the denominator and so your modelling diffusion process in this particular case akin to inertial process.

You are assuming that particles are diffusing or heavy molecules are diffusing in a mechanism that is very similar to how inertial settling happens. So you are kind of modelling it as a sedimentation process it is another way to put it and this turns out to be a good way again to estimate the diffusivity of heavy vapours in a lighter gas or as I said particles in a gas or a liquid. So the other type of diffusion process that can happen is after the molecule has absorbed on a surface it has diffusion along the surface and in fact that is a very critical process in achieving the final state of the CVD film on the substrate.

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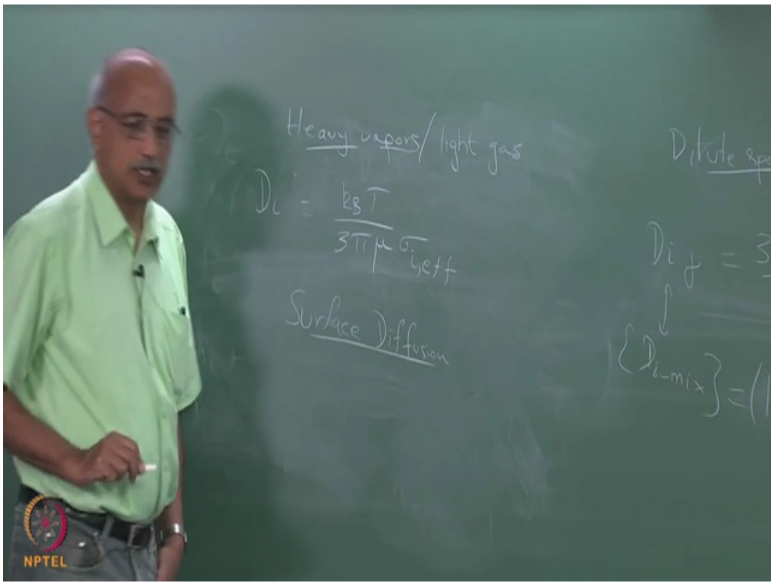

So when we talk about surface diffusion it has very different characteristics when you write the equation because in this case what you are really trying to model is the migration of an absorbed species one industry interstitial site to another you are trying to estimate the flux of that and from the flux you retry to estimate the diffusion coefficient. The diffusive flux associated with the species essentially jumping from one side to the next available site depends on, you know, several parameters including the activation energy that is required for the molecule to 1 interstitial site to another and also the number of attempted jumps.

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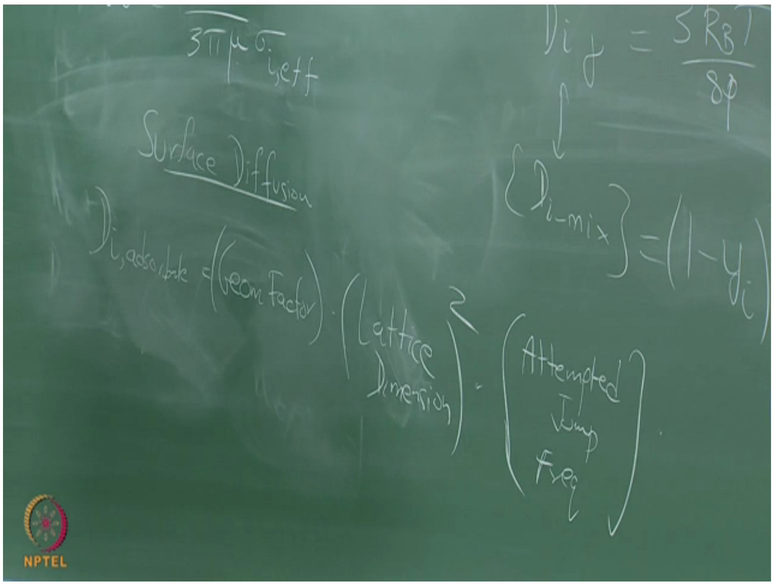

You know, how frequently does the molecule even attempt to jump. So in this case the diffusion coefficient for absorbed can be written as a combination of a geometric factor times the lattice dimension squared times an attempted jump frequency parameter times activation energy parameter.

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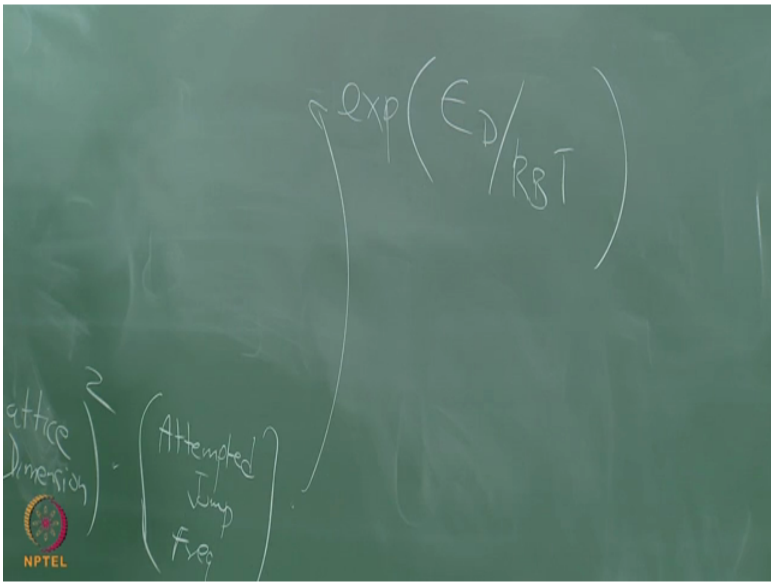

So the activation energy parameter can be written as exponential of Epsilon D over kBT, so it is the energy that is required that is that you have to get over if you want move one molecule from one interstitial site to the next one.

Now if you look at this expression the interesting thing of curves is that the geometry plays a huge role. For example if you have features on the substrate that make it difficult for diffusion to happen that can have an inhibiting effect on the diffusion process. On the other hand if you have certain well-defined diffusion pathways to begin with it will actually speed up the diffusion process. So all this is club into this geometric factor term.

The lattice that mention reflects the crystallinity of the substrate. A crystalline structure is one where the energy required to go from one interstitial site to the next can be quite high when energy barrier. So the degree of crystallinity which is reflected in a lattice dimension is another key parameter in determining the rate of diffusion because it attempted jump frequency.

Now that is a temperature dependent parameter, the higher the temperature the more will be the frequency of attempted jumps from one place to the other which is why if you have a CVD film on a surface and you want to make it more uniform, if you want the surface spread to be equal and if you want the film to be more adherent you typically raise the temperature.

Because it facilitates the moment of atoms across the surface after have been absorbed it just energised the atoms and makes them more willing to jump from one place to the next. Of course finally again as the temperature increases it becomes easier to overcome the activation energy barrier and move atoms from one place to the other.

So the thing to remember with diffusivity is that there is no single expression for it depending on the particular physical situation at hand, you know, whether we are talking about the diffusion of the precursor vapours to the substrate that is governed by a different flux diffusivity coefficient and then the actual migration of agglomerated or heavier atoms is governed by a different diffusion equation.

And finally once the diffusing molecule has been absorbed on the surface, its diffusivity on the solid surface is governed by a different equation in the affect of temperature and pressures are very different in each of these cases. For example surface diffusion is dominated by the temperature effects but pressure has very little influence whereas diffusion in the gas phase as we saw there is a very strong effect of pressure inverse effect.

Whereas the temperature effect is more moderate between T to the power 1.5 to 1.8 and in the case of heavy vapours again the temperature effect is quite significant but pressure is not, okay. By the way I do not think you need to remember all these actual equations but what you should recollect some of the (()) (33:53) dependencies, you know, how does viscosity, thermal conductivity and particularly diffusivity depend in various situations on system parameters like temperature, pressure and concentrations and so on.

Okay, so what we have quickly gone through in this lecture is, ways to estimate the constitutive coefficients particularly the viscosity, thermal conductivity and diffusivity which needs to be plugged into conservation laws in order for us to be able to solve the equations and obtain velocity distribution the temperature distribution as well as the concentration distribution of the reacting and diffusing species. Once you have obtained these coefficients you can solve the reservation equations but in the case of CVD process obviously you need to focus on the mass transfer mechanisms involved.

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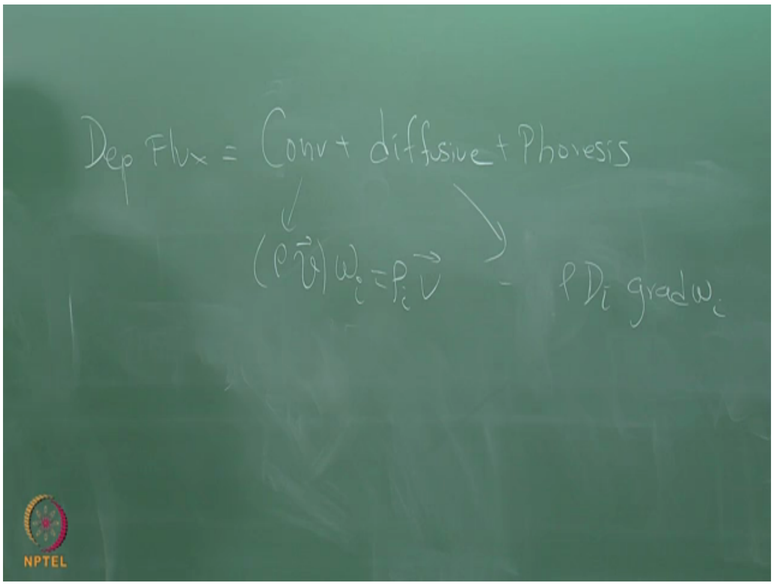

Dep Flux = Conv + diffusive + Phoresis

$(\rho \vec{v})\omega_i = \rho_i \vec{v}$ $\quad - \rho D_i \, \text{grad}\, \omega_i$

So if I look at the overall rate of deposition of a CVD film, the deposition flux it has that convective component to it plus a diffusive component to it, right? Mass can be transported by both convection and diffusion but there is also a third affect which is called Phoresis. So there are actually 3 phenomena that govern the overall mass transport process.

Now this is fairly obvious when we talk about convection, if rho V is the convective flux of the fluid system as a whole. If you take this and multiply this by Omega i which is the mass fraction of the ith species that gives you the convective flux of species i can also write this as rho i times V, this V is the vector. So the convective flux as is associated with molecules that are essentially following the motion of the fluid itself.

You know, they are just moving along with the carrier fluid but because the carrier fluid has the velocity and a mass associated with it there is a convective flux of the depositing species also and we just saw that the diffusive flux can be expressed as minus rho Di gradient in Omega i, so once you know the diffusivity of the diffusing species and you know it is a gradient you can calculate the diffusive flux.

The new term is the Phoresis term so what do we mean by that? What is Phoresis and why does it happen? And why is it important in CVD systems? Phoresis refers to the moment of species under the effect of an applied force. So it is distinct and different from the convective motion associated with the fluid flow itself.

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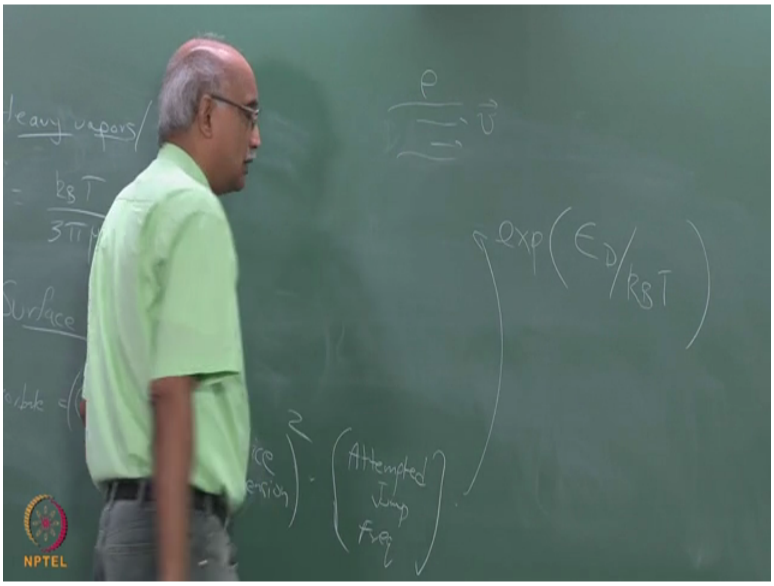

For example if you have a flow of a fluid with a certain velocity V and let us say that it is density is rho, rho times V gives you the convective flux and rho i times V gives you the convective flux of species i simply associated with the enforced flow of the fluid but supposing now I impose a temperature gradient across it. So this is T2 T1 where T2 is let say much greater than T1 then what happens?

Or let say that I impose an electric field across it, right? Or a magnetic field, or a pressure field, so I can on top of the basic flow situation I can impose various external fields and when I do that, that field induces a motion as well and it is more akin to a convective motion rather than a diffusive motion.

Another field that you can think of its just gravity, you know, in all our discussions of CVD we have kind of neglected gravitational force but it is present and it can have an effect. So the gravitational field itself induces a Phoretic affect, for example in a CVD reactor what would be some of the dominant Phoretic fields? Certainly thermal because particularly in cold wall reactor you know that the temperature gradient between the substrate and the walls of the reactor can be in the range of hundreds of degrees.

So the thermal gradient we do need to account for, pressure is typically not usually varying I mean the entire reactor will be set at a constant pressure, so there is no pressure involved convection within the reactor, magnetic fields very rare I am not aware of too many CVD reactors which use magnetic fields to drive the process. However electric fields are used because it has been found that by applying an electric field you can actually...

I am setting up an electric field gradient you can speed up a CVD process and so electrophoresis can be important effect. How about gravity? Is gravitational field an important parameter in CVD? Typically not because it is a diffusion-based process and gravity does not play a significant role in enhancing diffusion but when you start talking about very heavy molecules that are diffusing in a very light gas gravity can also become a parameter consider.

And then there is something called Diffusiophoresis which is a Phoresis associated with diffusion because as diffusion occurs there is a concentration gradient being set up that actually diffusion is conveying mass in one direction and according to the principle of mass conservation there must be an equal and opposite flow in the opposite direction and that is what we call Diffusiophoresis, it is also known as Stefan flow, so that is another parameter that can influence your net deposition flux.

So what we will do in the next few classes is, really concentrate on this Phoretic phenomena, what are the different types of fields that can be applied? And what are the velocities and fluxes associated with these Phoretic fields and you have to essentially learn to superimpose.

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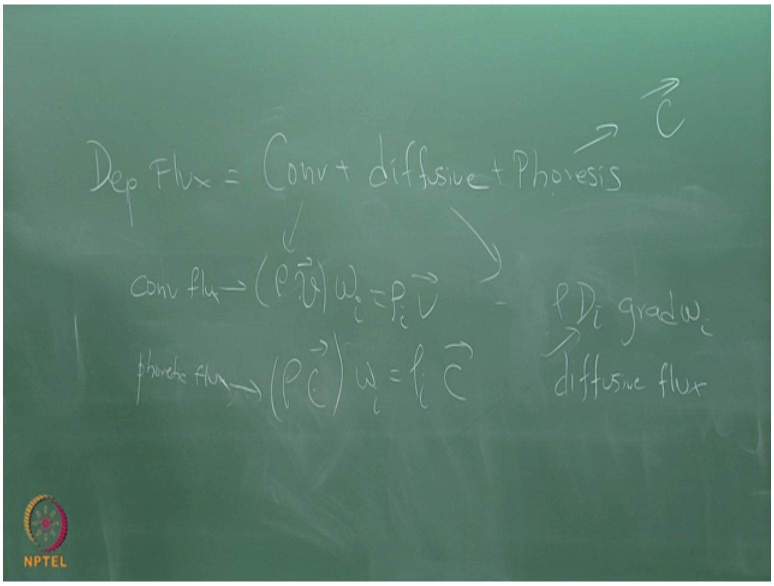

So for example associated with each Phoretic field there will be velocity C, so just like you have convective velocity V which induces a convective flux the Phoretic velocity C will induce a Phoretic flux which will be, you know, just like we have written the convective flux like this we would essentially write this as rho C times omega i or rho i times C as, so this is the convective flux and this is the Phoretic flux and of course this is the diffusive flux.

So the challenge really becomes how do you estimate this Phoretic velocity C for various fields? In some cases it is obvious in some cases it is not, so we will deal with that in a couple of lectures because it is the correction factor for deposition flux which if you are not careful and you neglect, you will not be able to estimate the deposition flux in a CVD reactor very accurately and that can lead to very misleading conclusions about the design and operation of your CVD reactor.

Okay, so we will stop at this stage, any questions? Okay, so I will see you at the next class.