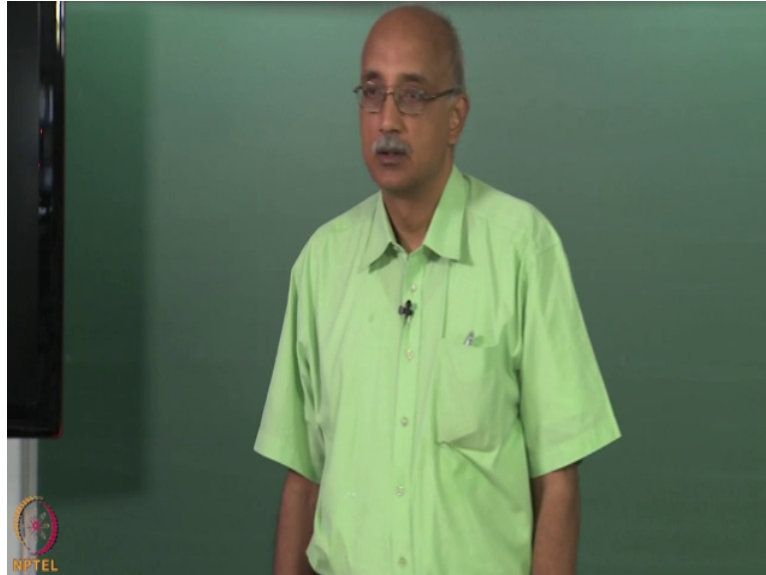**Chemical Engineering Principle of C V D Processes**
Professor R. Nagrajan
Department of Chemical Engineering
Indian Institute of Technology Madras
Lecture No 04
Basics of Chemical Equilibrium Calculations and Flow Dynamics

(Refer Slide Time 00:16)

Good morning. In the last lecture we were talking primarily about the chemical reactions that can happen in a C V D reactor and the fact that under the operating conditions of normal C V D reactor, the chemical equilibrium assumption is usually a valid one particularly when you are operating at high temperatures and high pressures.

But even under the simplifying assumption of chemical equilibrium prevailing, the calculation of the species composition present can still be very complicated because there are hundreds of chemical reactions going on. So what we said was that, in order to obtain the equilibrium composition of the system a simpler process would be to use a free energy minimization approach.
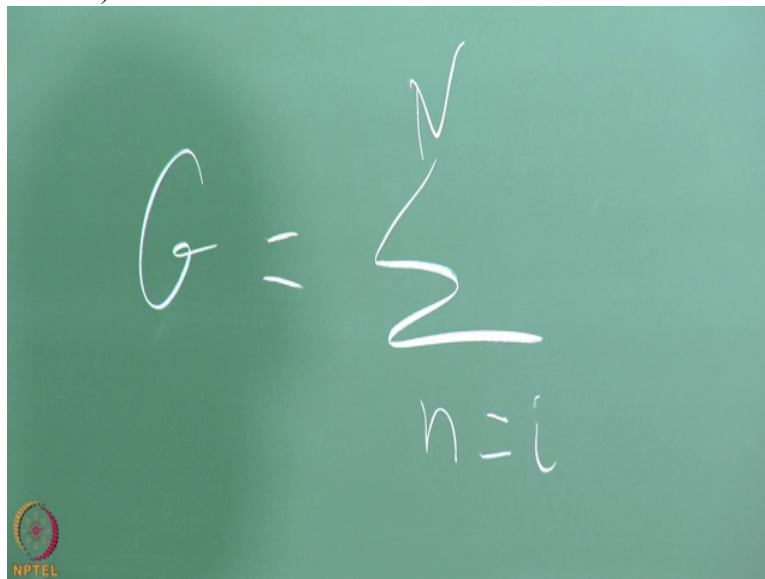
In any system as it approaches equilibrium conditions the free energy of the system is minimized just as entropy is maximized. So if you can write an expression for the free energy and then use a conventional minimization algorithm, you should be able to obtain the chemical equilibrium compositions.

So if you look at the expression for Gibbs free energy, Gibbs free energy calculation itself can be quite complicated in a multi-component, multi-phase system. Just remember that in a C V D reactor you have hundreds of species not only in the gas phase but also in solid phase and there could be some liquid formation as well.

If there is liquid formation in C V D reactor, it is usually unintended. But sometimes especially in a hot wall system you can have localized condensation of nucleated droplets for example. It becomes a three phase system.

So what that means is that when you consider the expression for the Gibbs free energy, you have to essentially summarize the free energy over all the chemical species that are present in the system
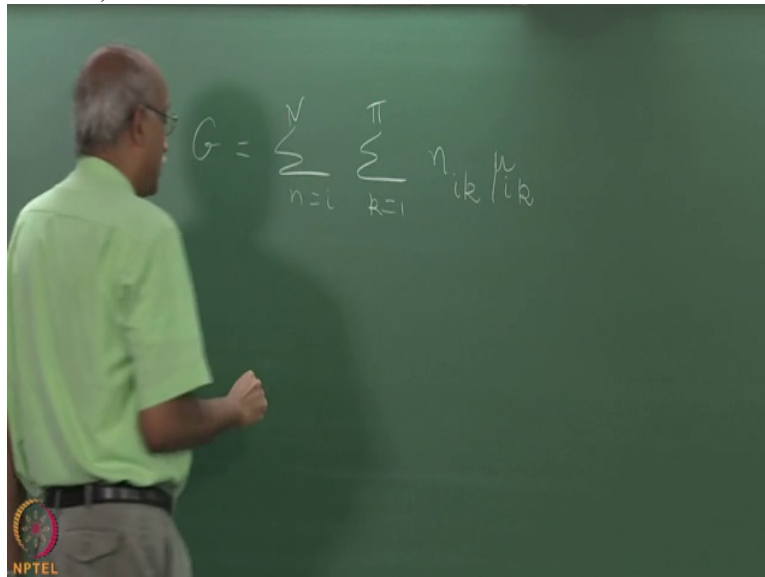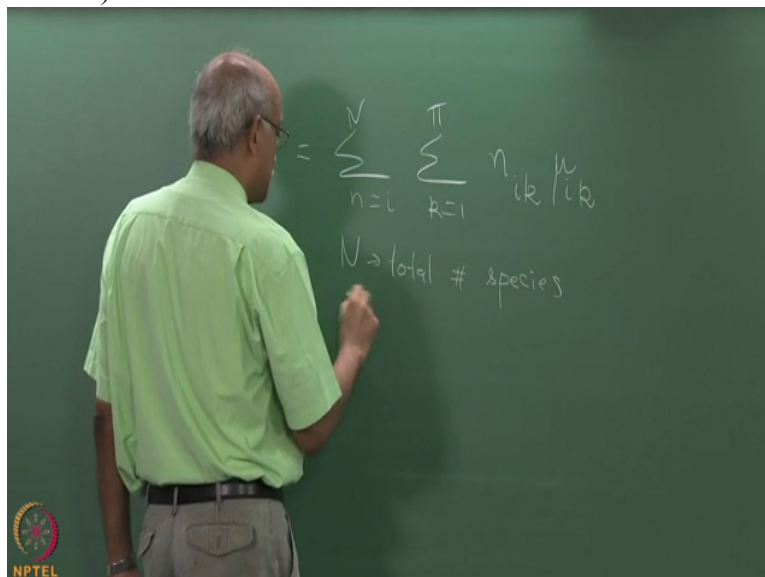
(Refer Slide Time 02:31)

$$G = \sum_{n=i}^{N}$$

and also over all the phases that are present in the system and then you write this as n i k times mu i k where

(Refer Slide Time 02:48)

$$G = \sum_{n=1}^{N} \sum_{k=1}^{\pi} n_{ik} \mu_{ik}$$

again, N is the total number of species,

(Refer Slide Time 02:57)

$$= \sum_{n=1}^{N} \sum_{k=1}^{\pi} n_{ik} \mu_{ik}$$

$$N \rightarrow \text{total \# species}$$
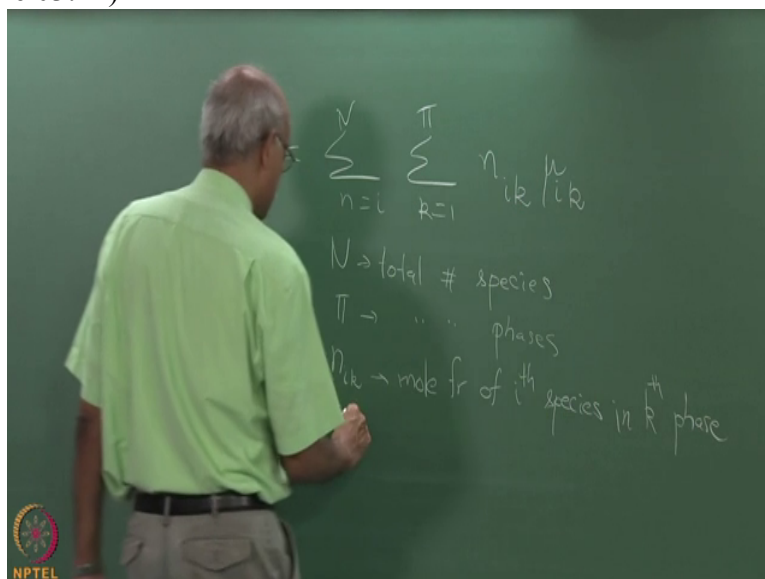
pi is the total number of phases,

(Refer Slide Time 03:03)
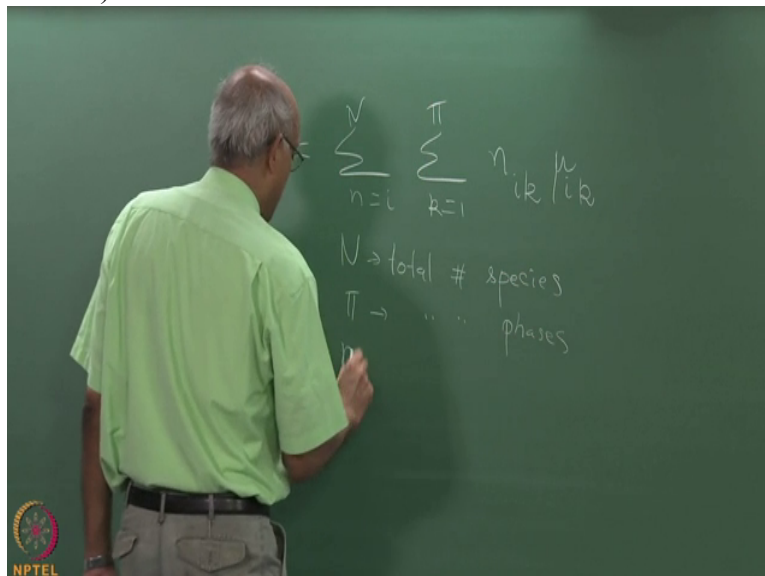
N i k is the mole faction of ith species in the kth phase

(Refer Slide Time 03:22)

and mu i k is the chemical potential of the ith species in the kth phase, Ok.

(Refer Slide Time 03:36)

So you write the expression for G and you minimize G to obtain n i k. How do you, you can further expand this and write this as this is equal to summation n equal to i to n, k equals 1 to pi, n i k and you can write mu i k in terms of the free energy of formation of species i plus R T ln, ratio of, so the delta G i

(Refer Slide Time 04:30)

k is the free energy of formation of species i in phase k and the f values are the fugacities, so f i k is the partial fugacity of species i in phase k and f i

(Refer Slide Time 05:00)

$$= \sum_{n=1}^{N} \sum_{k=1}^{\pi} n_{ik} \left[\Delta G_{i,k}^{f} + RT \ln \frac{f_{ik}}{f_{i}^{0}} \right]$$

free en of formation
of species in phase k

fugacities

zero is the fugacity of pure species i.

So once you have written it this way, delta G f is typically available in various handbooks. And so you can essentially, I mean in order to solve the system of equations a, you need to have a good numerical algorithm and actually the technique that is most widely used is what is known as direct search optimization which enables you to home in on the global minimum very quickly.

One thing you have to be watchful about is that because the expression for free energy is quite complex, you, there are many local minima. So you have to be able to differentiate between the local minima and the global minimum and home in on the global minimum. So you need to choose numerical techniques that essentially allow you to do that.

There are commercial packages by the way which have been written for the purpose, the one that I have used a lot was actually written by N A S A, it was back in the eighties, it is called the N A S A C E A program, I think it stands for chemical equilibrium analysis program. It is freely downloadable from the web but even the more conventional packages like Chemkin also have modules that deal with calculation of equilibrium compositions using the free energy minimization approach.

The other part of this is you need to have a good database. Because of the thermochemical properties of all possible species in the system because that is really what this right hand side

is. For every i you need to know these values. What is delta G, f i, and f i, and f i zero, for species present in various phases like gas, liquid, solid and so on.
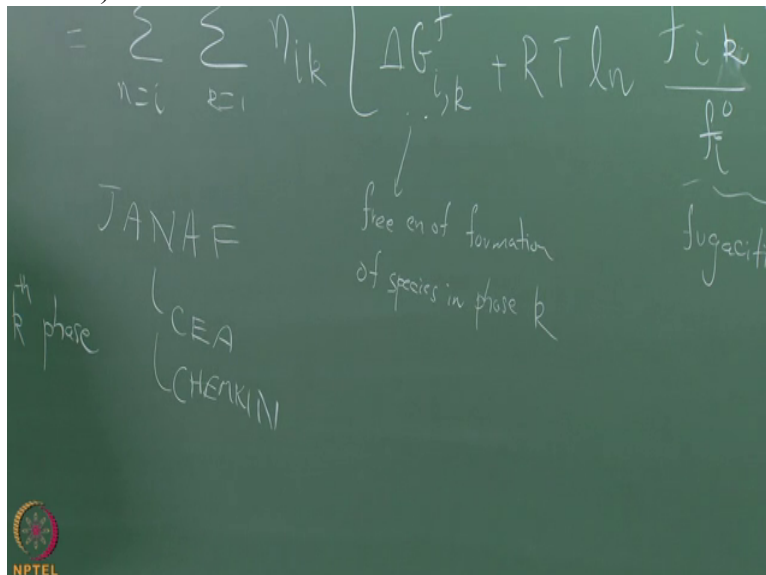
So you need a very extensive thermochemical database. And there is something called the J A N A F thermochemical database which is coupled with programs

(Refer Slide Time 07:09)
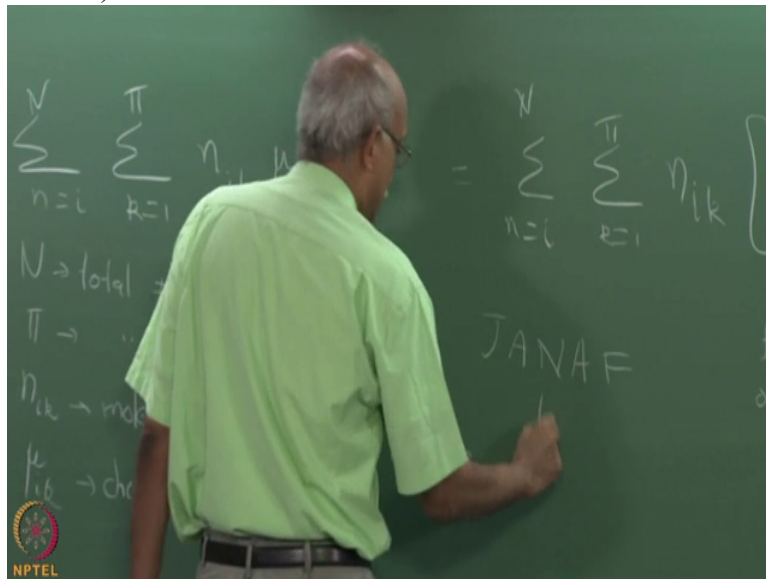
like C E A and Chemkin and there are few more packages. Actually if you go

(Refer Slide Time 07:20)

on the web and just search for free energy minimization you will be surprised that how many hits you get. The people have really spent a lot of time coming up with very efficient numerical algorithms for doing this but where they all succeed or fail is in the completeness of this database.

Because unless you have a good way to a, accurately estimate the thermochemical properties of the species and b, know all the species that are present in your system this method of solving will not yield you correct answers at the end. For example if you severely underestimate the number of product species that can form then obviously your analysis is going to be incomplete. And sometimes you can overestimate it as well.

So the, the way that these programs work, they start with an overestimation approach. They basically take the elements that are present, look at all possible combinations of the chemical elements and propose that all these chemical species can be present in the system. And then they go through this free energy minimization algorithm and pretty soon you can start weeding out species that are very unlikely to form.

And then you start kind of homing in on the right set of components. That is a better approach than going the other way where you start with the limited number of species because that can lead to these local minima type of problems. You may think that you have free energy minimized solution but it may be only because you have taken an incomplete set of chemical species to consider.

So just as important as the selection of your numerical algorithm is the selection of your database with which you are going to do your analysis and also your identification of possible species that can be present in the system. So you need to know something about the process. This approach is more of what I would call more of an engineering approach where you do not just treat the C V D reactor as a black box and do this entirely mathematically.

If you know that certain species are likely to form, you can actually force the program to treat those as more likely to form than other species. So that way essentially the convergence would be faster. So you can use a few tricks like that depending on your insight into the system to get your results in a more efficient manner.

Now what are the, in any minimization algorithm as you know, there have to be constraints, right? So what would be the constraints in this case? Can you think of some?

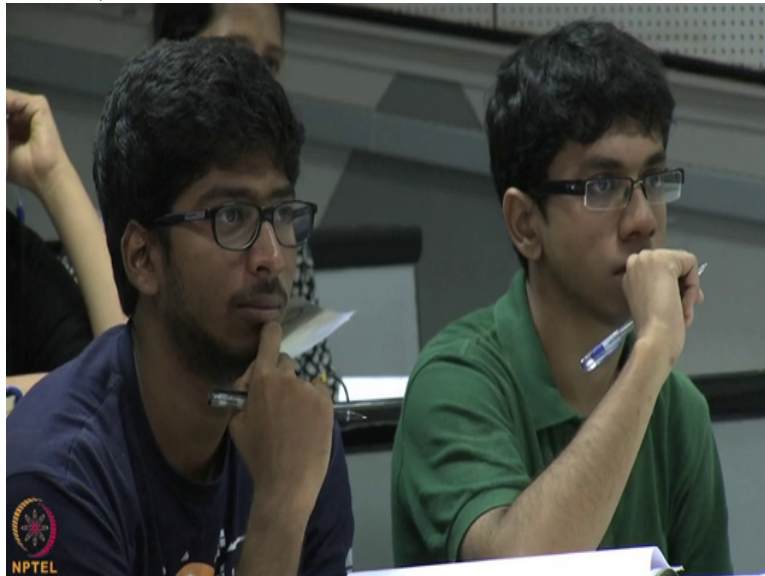(Professor – student conversation starts)

Student: n i k is greater than zero

Professor: Yeah, the obviously, the number or the mole factions of the species have to be non-negative, right. That is one constraint.
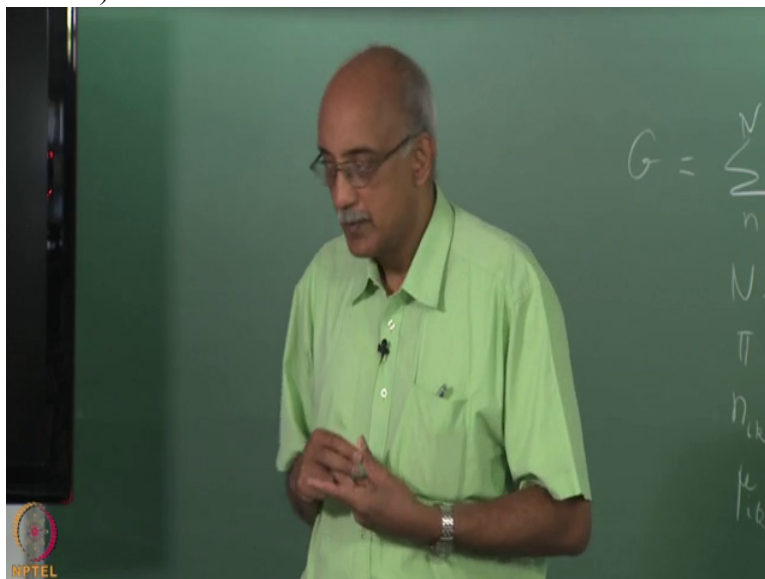
(Professor – student conversation ends)

The other

(Refer Slide Time 10:09)

is mass conservation. So when
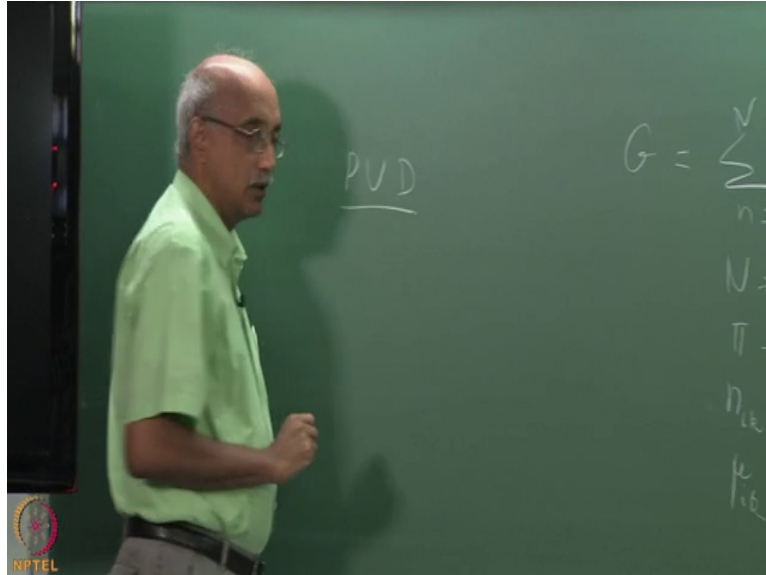
(Refer Slide Time 10:12)

we talk about mass conservation there is where the differentiation between P V D and C V D becomes very evident. In physical vapor deposition there is no transformation of one species

into another, right if you put in S i H 4 in a physical vapor deposition reactor it will stay as S i H 4. There will be no conversion to various other compounds in the system.
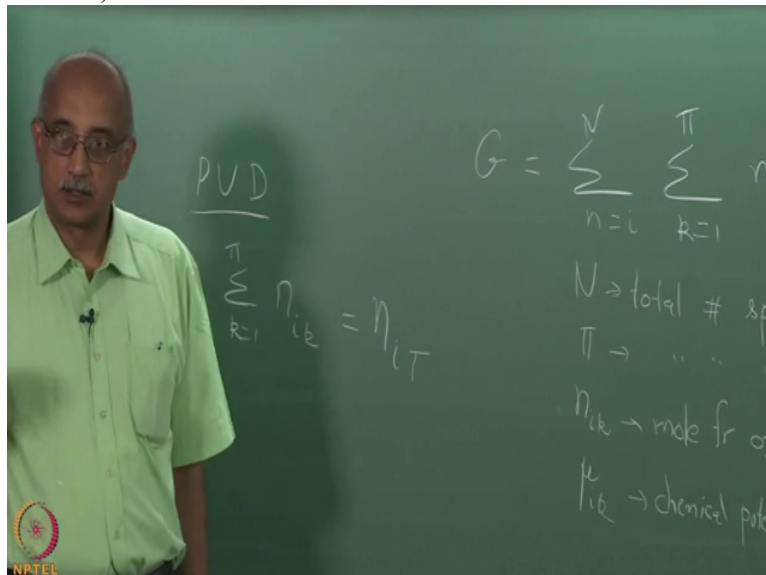
So in that case the imposition of the mass constraints would

(Refer Slide Time 10:42)

simply say that summation of k equals 1 to pi of n i k must be equal to some n i total which is

(Refer Slide Time 10:56)

the amount of species i that has been fed to the reactor through the feed stream, right? So the mass constraint is just placed on the species. In a C V D reactor, how would this constraint change? It is not enough. In fact this equality would not apply in a C V D reactor because the species would not stay intact, right? They will be transformed into other species.

So how do you handle that? How do you impose a mass conservation condition in a C V D reactor? Any ideas? What is it, even in a C V D reactor, what is it that does not change? What is it that cannot be created or destroyed?

(Professor – student conversation starts)
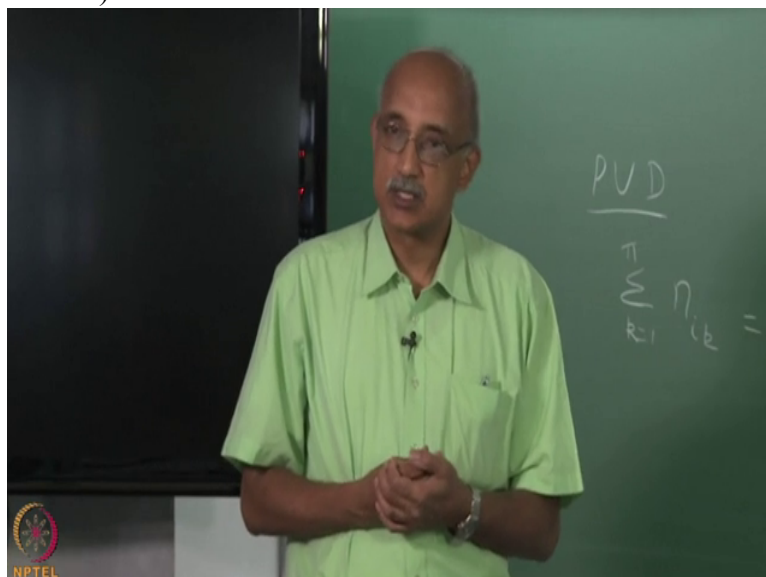
Student: Mass

Professor: Total mass.

(Refer Slide Time 11:44)

Student: Total mass

Professor: But that does not help us much.

(Refer Slide Time 11:46)

Anything else?

Student: Elements

Professor: Elements? Unless it is a nuclear reactor, right the total amount of elements that you feed into the system must remain. You cannot transform
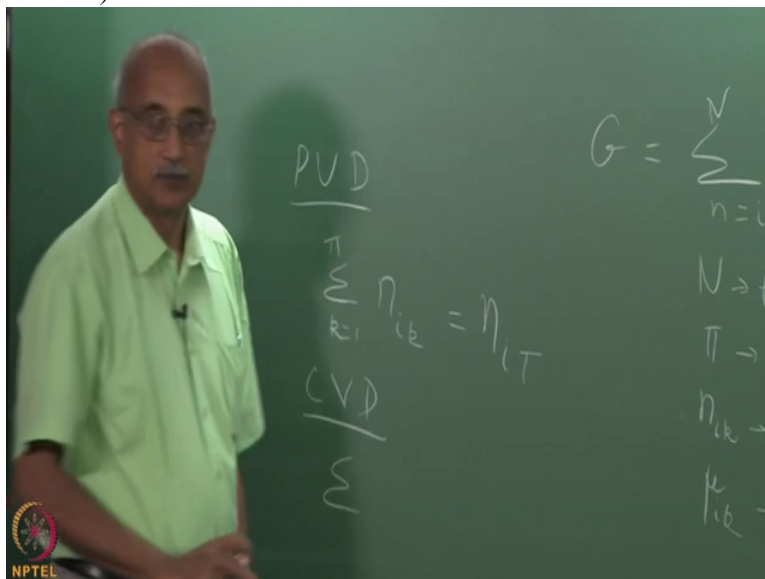
(Refer Slide Time 12:00)

one element into another.

(Professor – student conversation ends)

So in the case of the C V D reactor, the mass constraint is placed on

(Refer Slide Time 12:09)

elements and essentially the way you would write that is to say that the summation of elements, you essentially do the summation over all, actually you do the summ/summation, you do this for every element that is present. So you would still sum over n equals 1 to total number of species, capital N of a e i times N i k equal to some b e where a e i is

(Refer Slide Time 12:49)
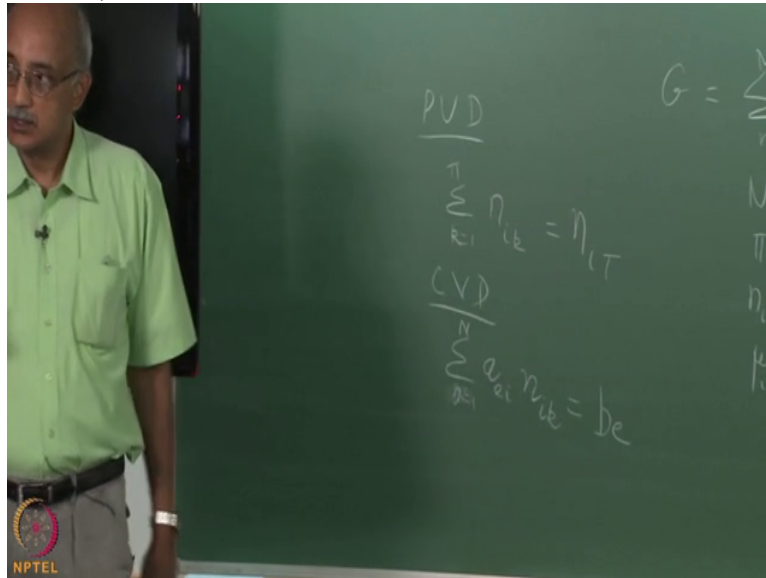
the mole faction of chemical element e in species i.

So when you sum that over all, and by the way this summation should also be over all phases, k equals 1 to pi summation n equals 1 to N and this is the total amount

(Refer Slide Time 13:11)
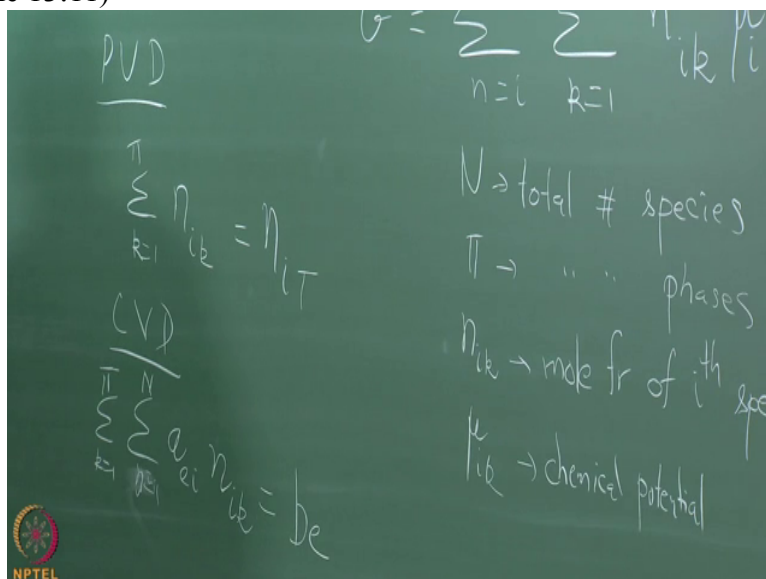
of that element that was fed into the system. So essentially a C V D reactor must obey element conservation principles, and total mass conservation principles where as a P V D

reactor must obey total mass conservation, element conservation and species conservation because species do not get transformed. So that is a key difference that, that you should try to remember.

So essentially given these constraints and the non-negativity constraints you can proceed to do a constraint minimization of the free energy and so the program will essentially give you a set of product compositions for a given, essentially what you feed into the program will be the feed composition and the operating conditions of the reactor, the temperature distribution and the pressure distribution. Once you feed that in, at each location inside the C V D reactor the free energy minimization algorithms will yield the equilibrium compositions prevailing under the local conditions.

Now if the program is running correctly and your reactor has been designed properly, through the entire reactor you should only see gas phase species and the second phase should only start appearing at the substrate. And therefore you do not really have to worry about multi-phase calculations through 99 percent of the C V D reactor space. So only the vicinity of the substrate that you are going to see a multi-phase situation happen and start
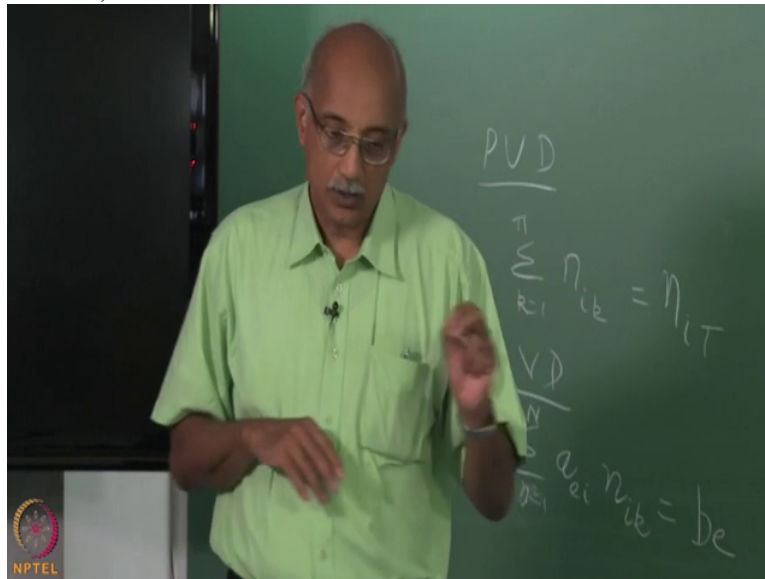
(Refer Slide Time 14:53)

condensing solid films on the surface.

These

(Refer Slide Time 14:59)

subroutines are also very good not only for pure condensates but also for mixed condensates. So you can have situations where instead of depositing a simple film of silicon, you may actually be depositing a composite film of silicon germanium for example. Here these algorithms can predict appropriate compositions but the database again becomes important.

You have to know about the phase equilibrium characteristics between the two condensed phases. You have to know when silicon and germanium form a compound, what does the phase diagram look like. And that data has to be fed into the database in order for the predictions to be accurate.

So the thing to remember is free energy minimization algorithm is a very elegant and very efficient method to achieve convergence towards equilibrium compositions but the predictions are only as good as the database. The stronger your database, the more comprehensive your database, the more confidence you have in the predictions.

But still even with an inadequate database, these predictions are likely to be more accurate that one where you try to assume certain chemical reactions. And then try to calculate equilibrium compositions based on that because you can never guess all the chemical reactions that are going to happen. And it is purely guess work, right. You do not really know what reactions are taking place. All you know is, these were my feed materials and this is my product composition. You do not really know how you got there, right? You can make certain assumptions but they are just likely to be wrong as they are likely to be right.

So bottom-line is if you are going to do chemical equilibrium compositions, the free energy minimization algorithm not only for a C V D reactor, in any chemically reactive situation where the conditions are such that you will have a large number of chemical species forming, you are much better off using a free energy minimization algorithm approach rather than something that requires you to specify reaction pathways.

Of course the chemical equilibrium assumption may not be valid in many reactions that you deal with. For example in the bio area, most reactions happen close to room temperatures because high temperatures will kill many organisms and so on. So in those cases, your reactions are very much rate limited. And this kind of a chemical equilibrium approach would not work.
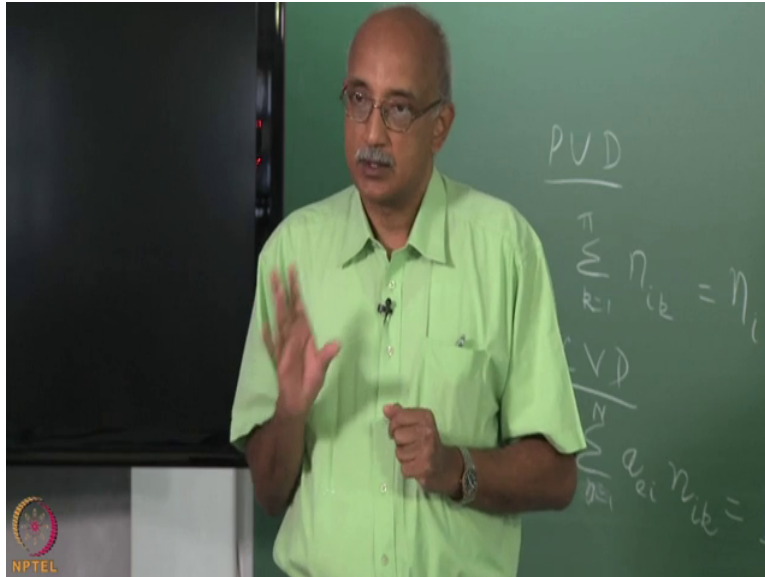
But in situations that involve high temperatures such as C V D reactors, combustion

(Refer Slide Time 17:41)

systems, even this incandescent bulb that I talked about earlier, these are all cases where there is a very high temperature, high pressure

and the likelihood of reaching equilibrium is very, very high. In such cases there is no question that the free energy minimization algorithm, it is the way to go.

Ok so any questions on that before we move on to a discussion of some basic transport phenomena? I will also send some reading materials on the free energy minimization approach today and take a look at it, you know, review it and then if you have any questions, you know, may be bring them up in the next class.

So now that we have a reasonably good handle on how to deal with the chemistry in C V D reactors, the second important aspect is the flow dynamics. Now the reason that flow dynamics are important is not only because they establish local pressures, local velocities and local temperatures but also because they have a very direct influence on the transport of the reacting species into the reactor and then the transport of the daughter species to the vicinity of the substrate on which you are trying to deposit the C V D film.

So it is very important to characterize flow dynamics. And the simplest way to do it is to assume that the C V D reactor is essentially a tubular reactor in which flow is happening in laminar flow conditions.

As I mentioned earlier, most C V D systems are designed to have laminar flow. And therefore making the assumption of laminar conditions is perfectly valid. So when we look at the C V D reactor, the way we have sketched it in the past is something that looks like this.

So there is a substrate

(Refer Slide Time 19:44)
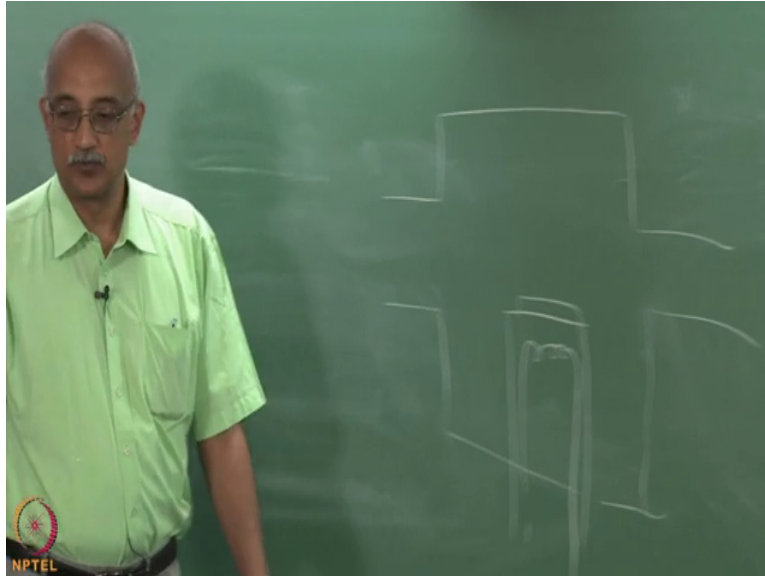
which is mounted into the reactor such that deposition happens on the substrate and it is provided some source of energy whether it is thermal or laser or photochemical or whatever and the flow typically happens in this direction and the exit gases leave in this direction. So we are trying to model the C V D reactor from a transport viewpoint. The simplest way to model it is just assume that this is a tubular reactor

(Refer Slide Time 20:15)
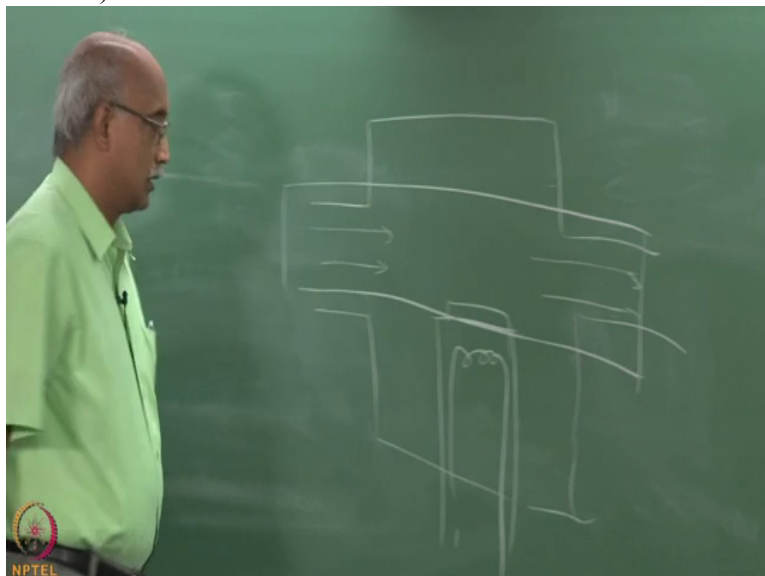
and that flow is happening through this reactor.

And the other assumption which is very important to modeling of transport phenomena inside the reactor is to assume that the flow enters the reactor essentially as a plug flow most likely,

because hopefully your flow input is designed such that you have plug flow going into the reactor but by the time it leaves the reactor, what kind of profile do you think the velocity will have?
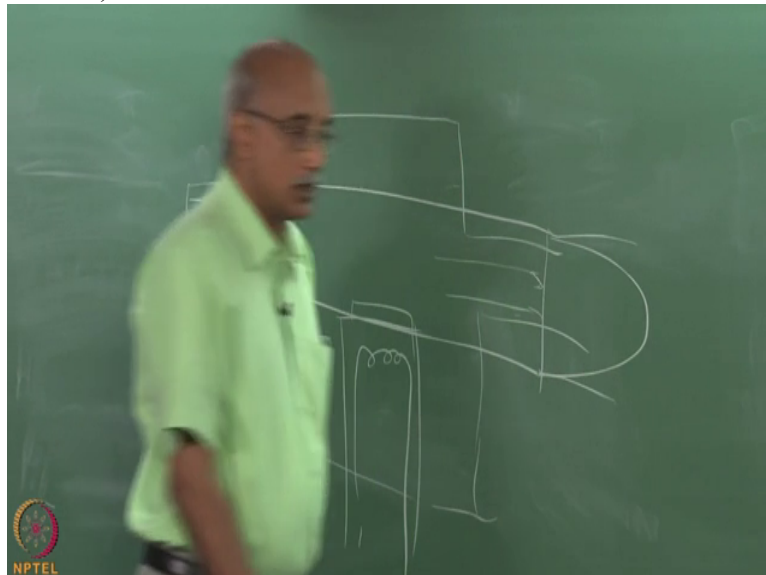
Remember we said it is going to be laminar, so in a tubular flow under laminar conditions what kind of velocity profile would you get?

(Professor – student conversation starts)

Student: Parabolic

Professor: Parabolic, right? So the basic assumption in all of our transport modeling is that

(Refer Slide Time 21:03)

flow will enter as a plug flow and leave as a parabolic flow.

(Professor – student conversation ends)

Under what conditions is this assumption likely to be valid? What is the major assumptions you make about C V D reactors, and by the way the assumptions I am going to talk about will not apply under special conditions such as extremely low pressure C V D reactors, plasma enhanced or plasma assisted C V D reactors because some, the first assumption we will make is continuum. So what does

(Refer Slide Time 21:49)
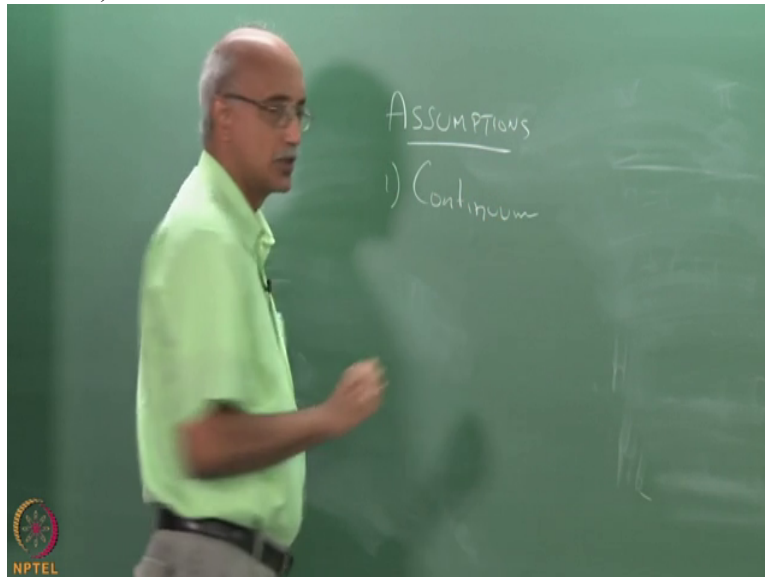
continuum flow mean? What are we saying when we say there is a continuum flow inside a system or a reactor, what are we talking about?

(Professor – student conversation starts)

Student: 0:22:00.1 of the system is not equal to the length...

Professor: Well, 0:22:10.1 is just not equal to

Student: The order of...

Professor: Much, much less. So the mean free path
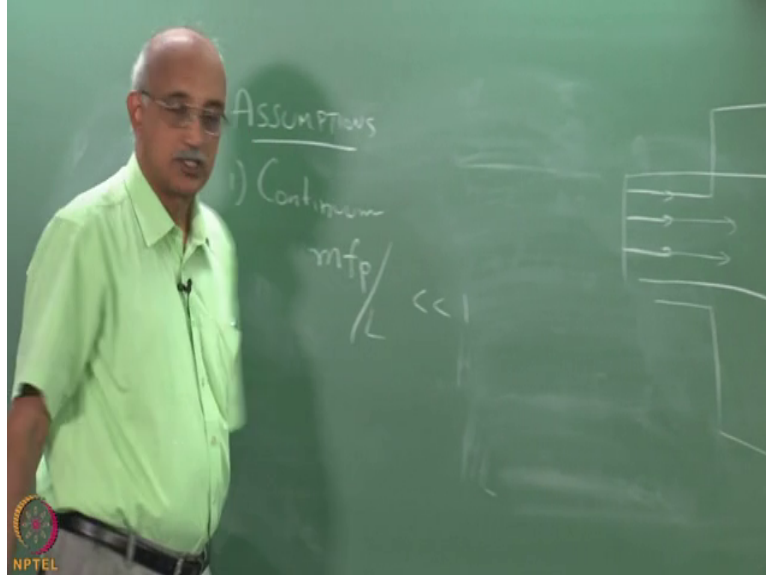
(Refer Slide Time 22:14)

divided by the characteristic dimension of the reactor, let us say that we take that as the length of your substrate.

(Professor – student conversation ends)

So this must be

(Refer Slide Time 22:29)

much, much less than 1. So that will yield continuum conditions and by the way, all the equations that you are familiar with, that you have studied in your courses have all been derived under continuum conditions. You know, whether you talk about Navier Stokes equations or Bernoulli equations or any mass, momentum, energy conservation equations that you have dealt with in your coursework so far have all been under continuum conditions, right? Have you dealt with free molecular flow or transition flow? Ok

The second assumption that we will make is that it is incompressible. What does that mean?

(Refer Slide Time 23:18)
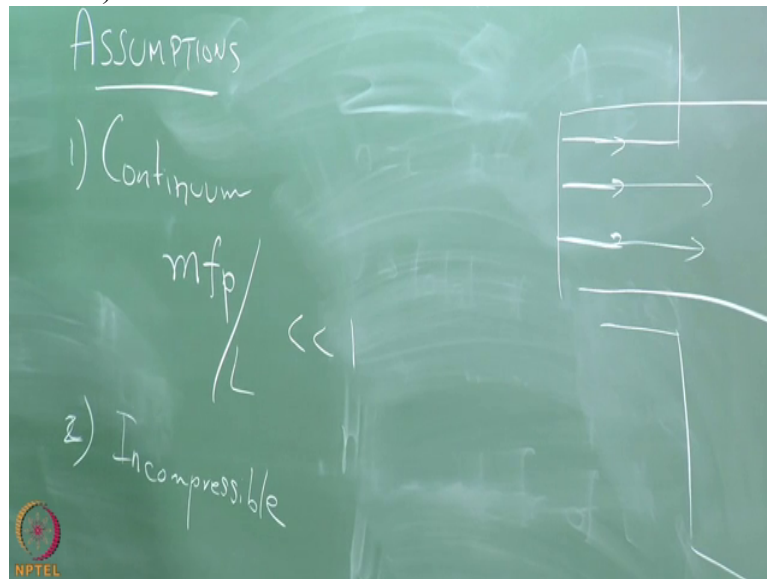
What do we mean when we say incompressible?

(Professor – student conversation starts)

Student: Density does not change

Professor: Density does not change with?

Student: Pressure

Professor: In the system essentially density stays constant not with time but actually along streamlines, right? It can actually change with time by the way.
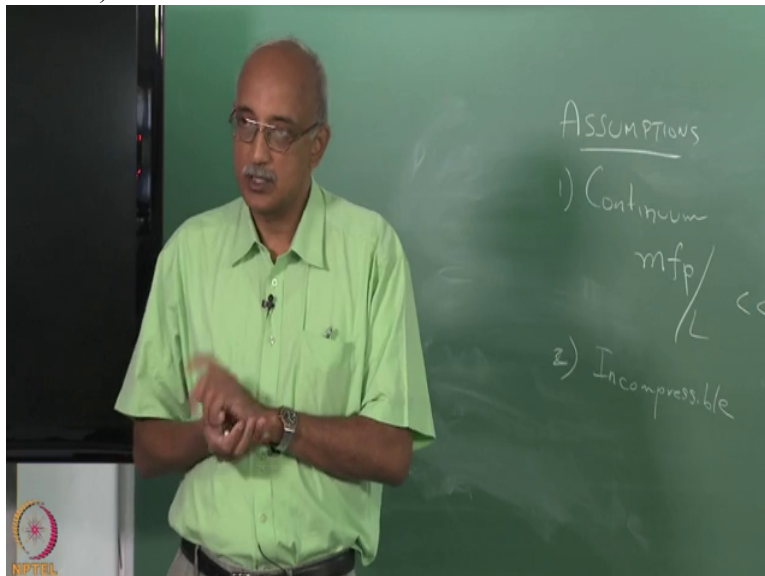
(Professor – student conversation ends)

In incompressible system, density is allowed to change with time. It is only it is not allowed to change with streamline flow. But, so what decides whether the flow is compressible or not? Is there something you can claim based on the velocity of flow?
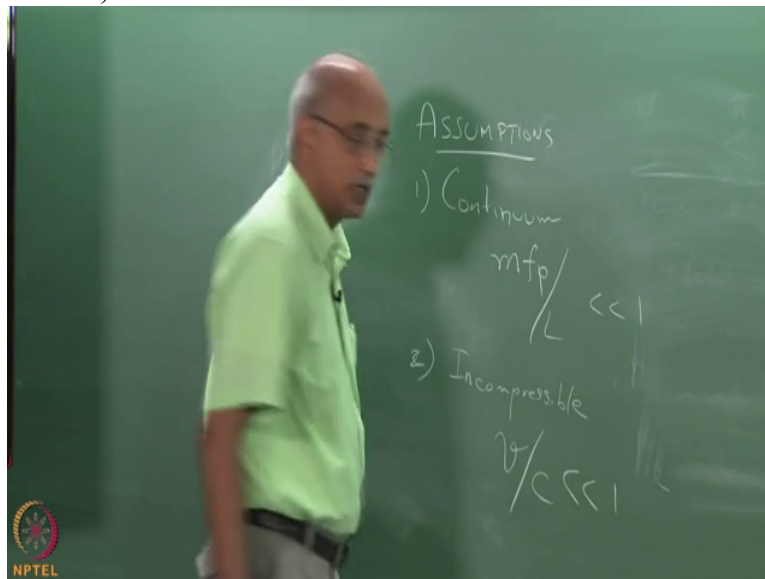
(Refer Slide Time 23:55)

(Refer Slide Time 23:58)

The requirement for incompressible flow is that the velocity of fluid flow divided by the
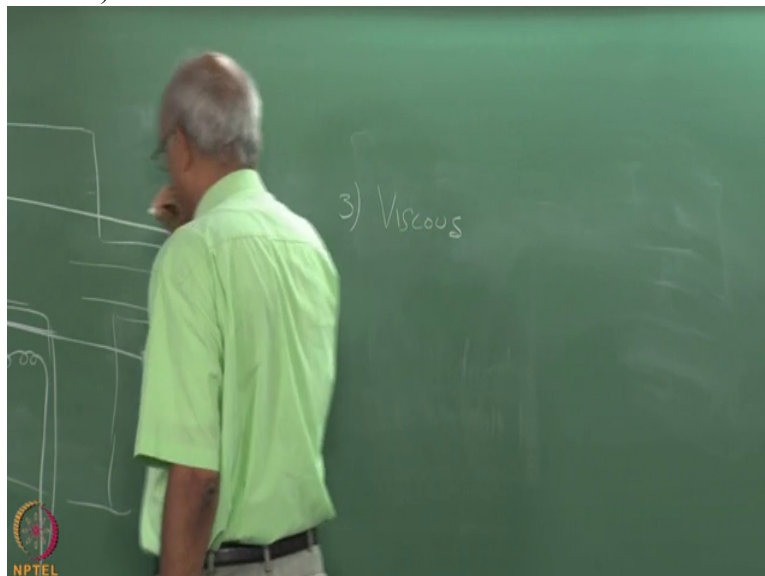
(Refer Slide Time 24:05)

speed of sound must be much smaller than 1, Ok.

The third assumption we will make is it is a viscous flow.

(Refer Slide Time 24:21)


What does it mean? It just means that fluid has a finite viscosity. And in fact, that is what you need in order for this structure to be obtained, right. If you have a completely inviscid flow you would not have a parabolic structure. So we are assuming that the fluid has a finite viscosity which leads to the parabolic flow.

Another assumption that we have mentioned even earlier is laminar.

(Refer Slide Time 24:52)
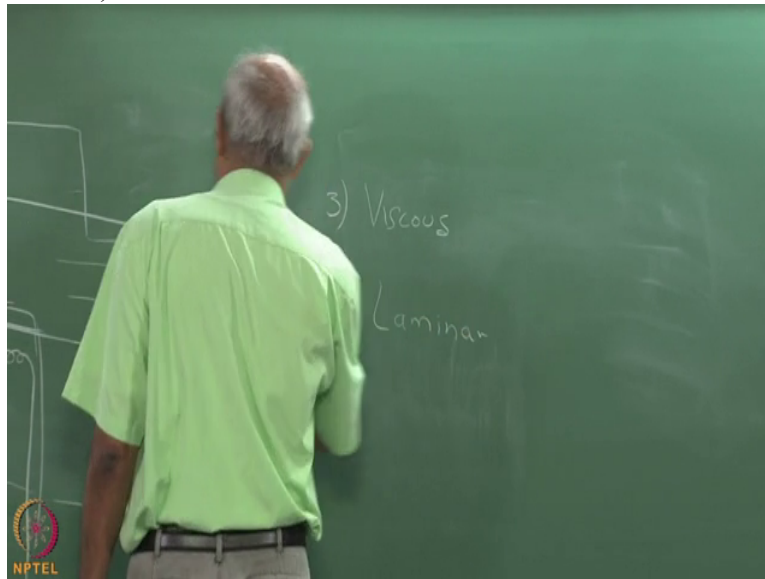
So again the laminar flow is what gives you that parabolic configuration but in terms of the surfaces that the fluid comes in contact with, what does it imply? What do we mean when we say laminar flow?

(Professor – student conversation starts)

Student: 0:25:07.8

Professor: Right, so when we say the laminar flow, the flow under, the entering flow is that a uniform velocity of u infinity and that velocity drops to zero everywhere along the solid surfaces that the fluid comes in contact with.

Now in a conventional C V D reactor, obviously the transition from laminar to turbulence is decided by what number?
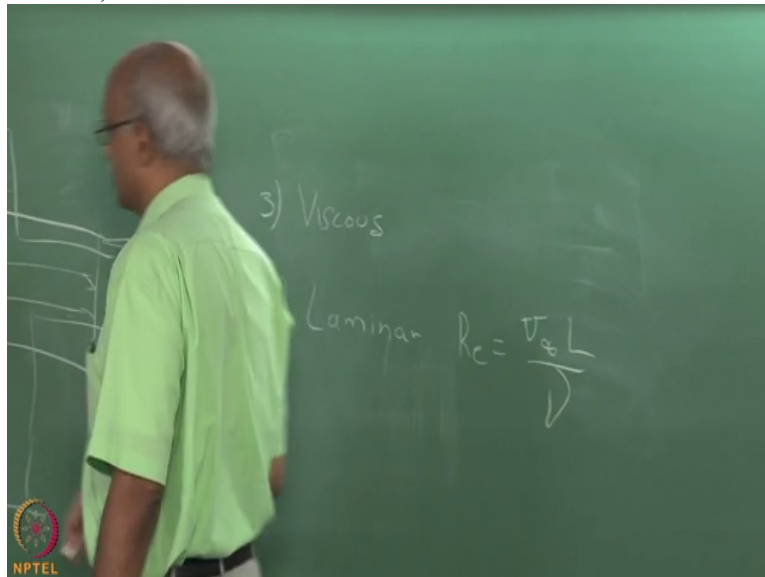
Student: Reynolds number

Professor: Reynolds number, right?

(Professor – student conversation ends)

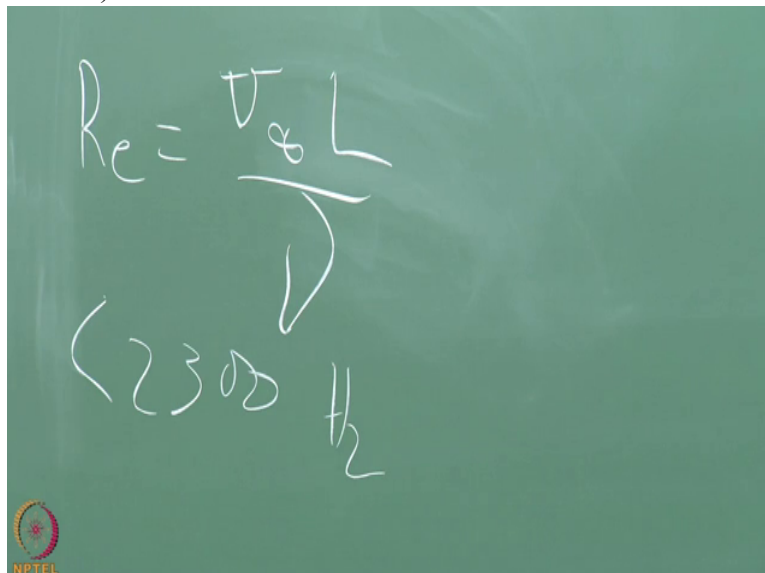So let us say that you have a Reynolds number which is defined as some u infinity L by mu where

u infinity is your entering velocity and nu is your kinematic viscosity which is mu by rho, dynamic viscosity divided by density, this number has to be less than 2300 in a C V D reactor with hydrogen as the primary diluant.

As long as you keep the Reynolds number below 2300
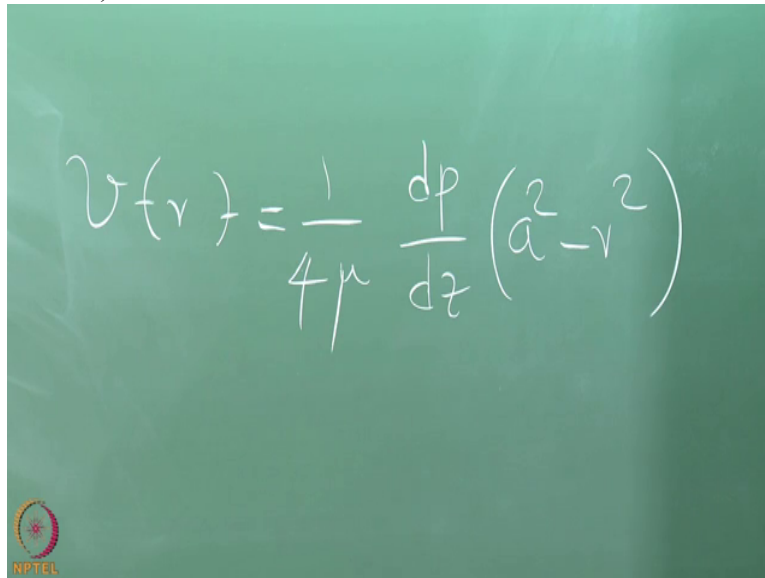
in a C V D reactor with hydrogen as the flowing gas you can be sure that laminar flow will be obtained. Obviously the condition for laminar flow will change depending on the fluid so this is only for the case where hydrogen constitutes 90 percent of the fluid that is, that is flowing. So under such conditions how do we write an expression for the parabolic flow? Do you remember?

So you write it as v as a function of r being equal to 1 by 4 mu times d p by d z times a square minus r square where mu is the dynamic viscosity, d p by d z is the pressure variation in the normal direction
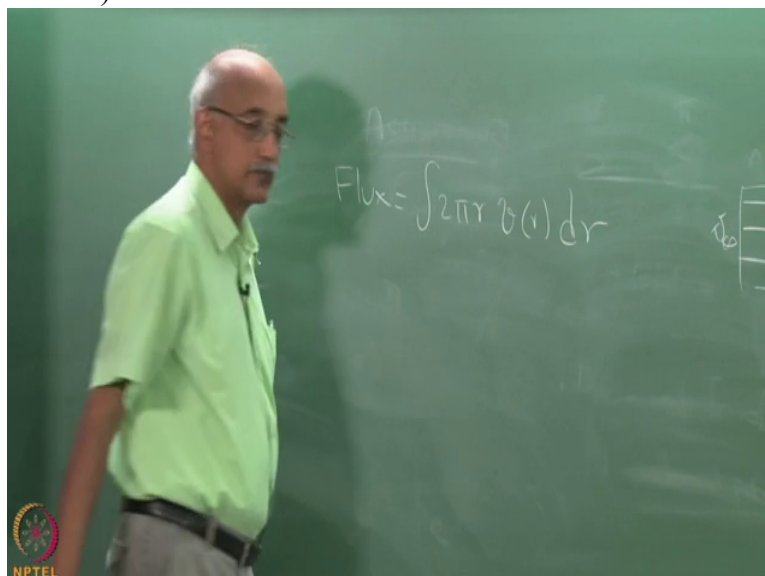
$$v(r) = \frac{1}{4\mu} \frac{dp}{dz} \left(a^2 - r^2 \right)$$

and a is your tube radius and r is the radial distance.

Now once you have the expression for v of r, you can also calculate the flux as integral of 2 pi r v of r d r.

$$Flux = \int 2\pi r\, v(r)\, dr$$

So that is essentially the area times velocity will give you the mass flux. And the other critical parameter here is obviously the boundary layer thickness.

As we mentioned earlier it is the diffusion through the boundary layer that ultimately transports the reacting species as well as the species that should be adsorbed on the surface to the substrate. So the final resistance to that is the diffusion through the boundary layer.

So the boundary layer thickness becomes an important parameter. The variation of the boundary layer thickness as a function of x distance is what, I mean what is the, what will be the dependence of boundary layer thickness on x? Should it go as delta is proportional to x or x to x squared or x to the power half?

(Professor – student conversation starts)

Student: Half

Student: Root

Professor: See we are talking about the flat plate, flow past a flat plate right, and so we are trying to understand how this boundary layer thickness

(Refer Slide Time 28:53)
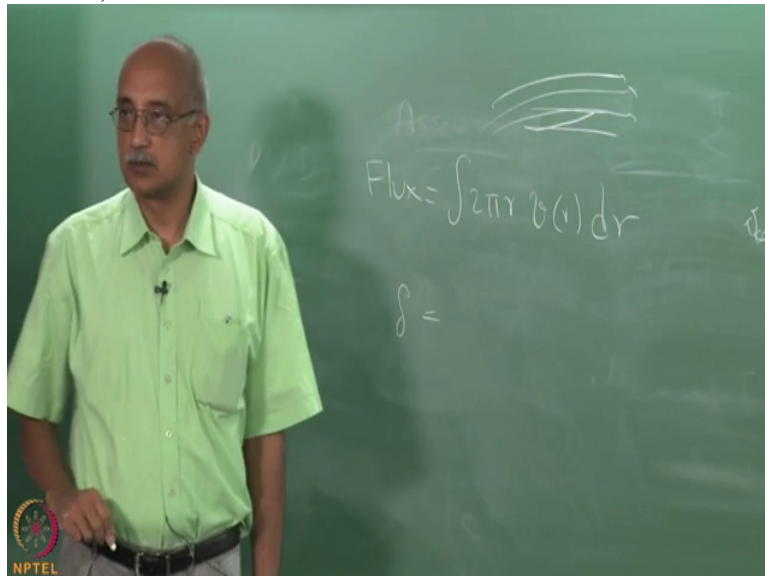
will change as a function of downstream distance x. What would, what would the shape look like? Will it look like this, or will it look like this or will it look like this?

Student: 0:29:08.6

Professor: The second one, right? So the essentially the dependence is, it is proportional to square root of x where x is this distance and this is your boundary layer thickness.

Or numerically this can be written as 5 times square root of u infinity x by nu.

(Professor – student conversation ends)

Now

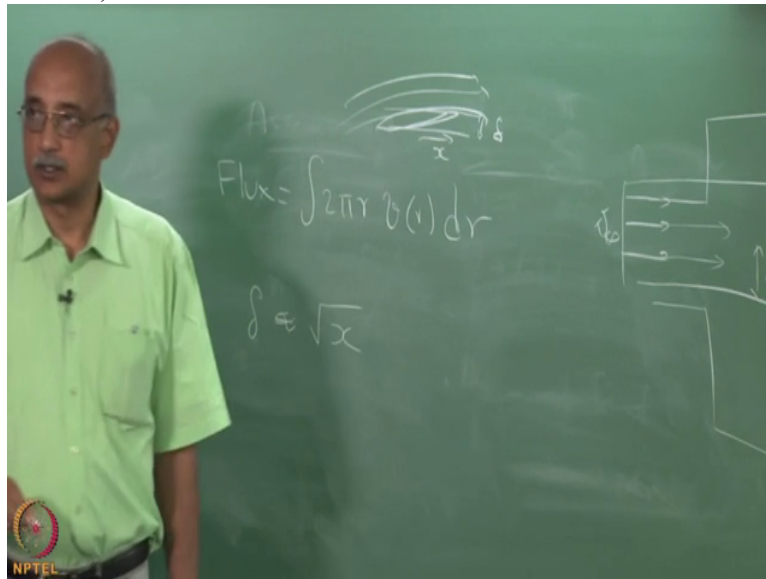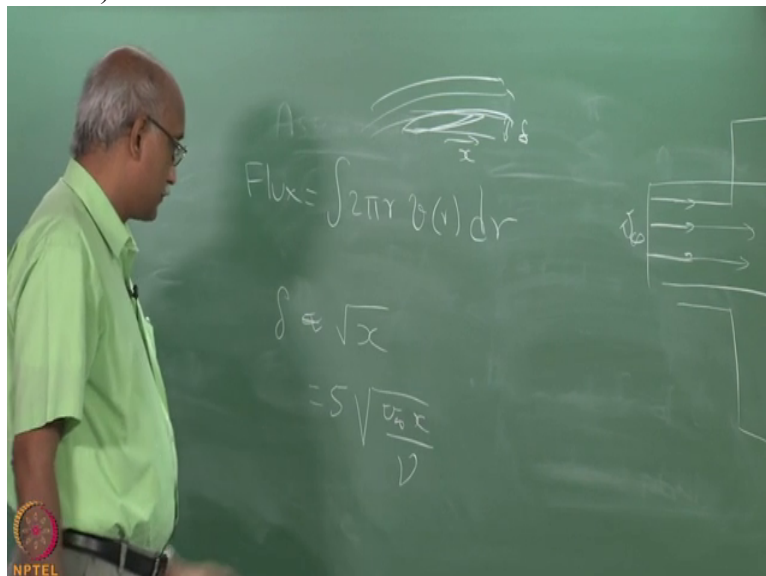this is an important equation because it tells you that a, there is going to be non uniformity in the boundary layer thickness which we talked about earlier, right as flow occurs over a flat plate where the normal to the plate is perpendicular to the flow direction, the boundary layer thickness will change as x to the power half. So it is important that we recognize the fact that the boundary layer thickness will look like this.
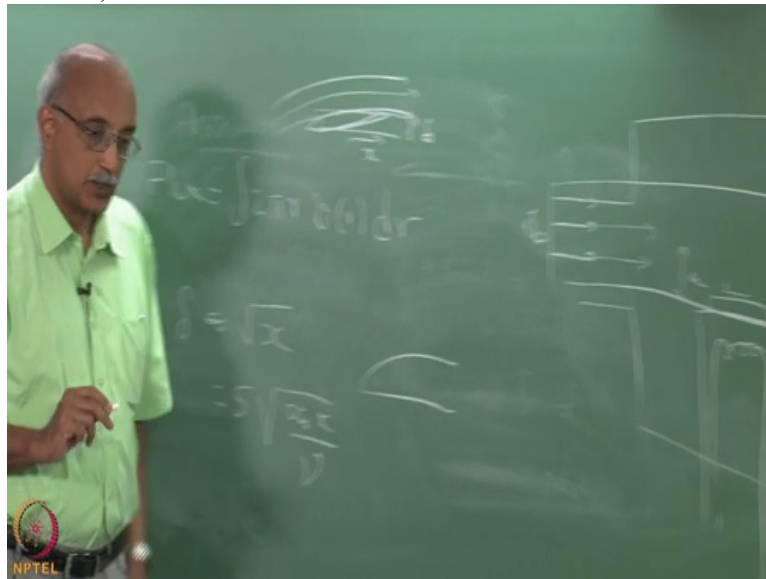
So if your transport of the, the reactive species is going to have to happen through this boundary layer thickness then clearly the rate at which the species are going to arrive at the surface on the leading edge is going to be very different from the rate at which the species are going to arrive on the surface of the trailing edge. It could be much slower at the trailing edge which again leads to non-uniformity, right?

Earlier we had discussed this non-uniformity in another context which is that, if we have a pure species that is being fed into the system, the concentration of the species will be much higher at the leading edge and it will start trailing towards the trailing edge. And we said that you fix that by essentially using a diluant. So instead of feeding in S i H 4 at 100 percent concentration, you feed in S i H 4 at 1 percent concentration with 99 percent hydrogen as diluant and that only, but that only keeps the free stream concentration of silane constant across the length of the substrate.

But it still does not address this issue that towards the trailing edge of the substrate you are going to have a drop-off in the diffusional depositional rate compared to the leading edge of the substrate. So how do you address that?

I think the suggestion that was given the last time was to tilt at an angle. That solution would still work in this case also. So by tilting the plate at an angle you can essentially force the boundary layer thickness to be much more uniform across the length of the boundary layer. Of course there are other solutions such as again rotating the substrate and so on.

Other approaches would include not flowing in the horizontal direction but as I mentioned in the earlier class, perhaps
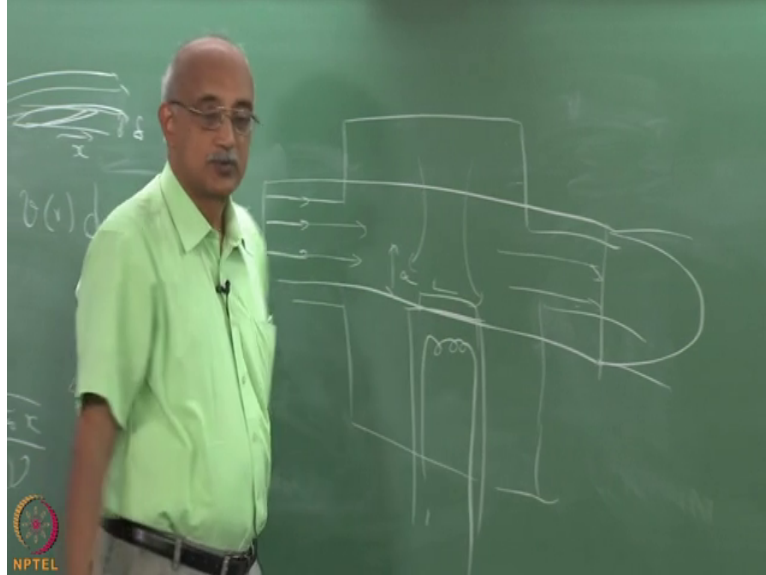
flowing it in a vertical condition to achieve stagnation flow. And so the flow dynamics, the point is that it does play a very significant role in how material is delivered to the surface. So this is, you know, important equation to keep in mind and make sure that we design the system in order to achieve the uniformity as well as rate of deposition that we are looking for.

So what happens inside the reactor; means we are introducing the flow as the plug flow. But it is exiting as a parabolic flow. Where does that transition happen? And does that have an influence on, again the flow dynamics and its impact on the deposition process? Where do you want the transition to happen? Do you want this transition from plug flow to parabolic flow, do you want it to happen upstream where the substrate is or at the midpoint of the substrate or downstream of the substrate?

(Refer Slide Time 33:07)
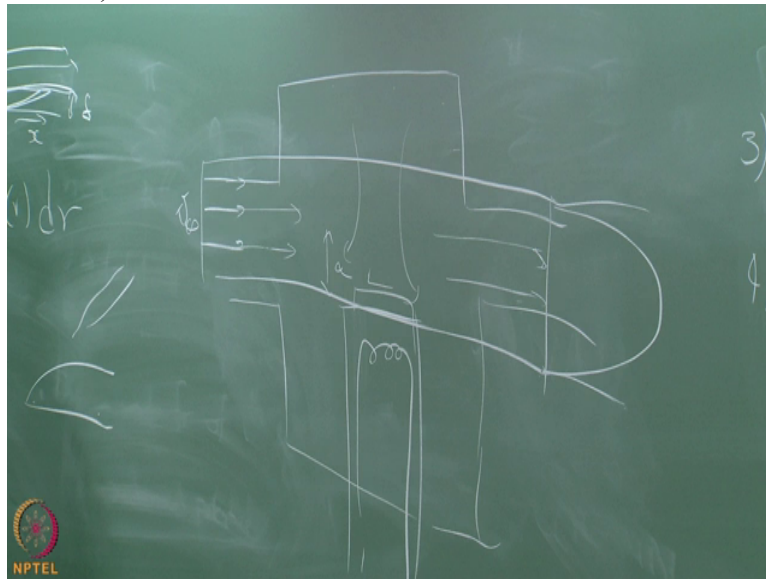
So you want it to happen downstream of the substrate. So you want the material essentially to follow plug flow across

(Refer Slide Time 33:18)
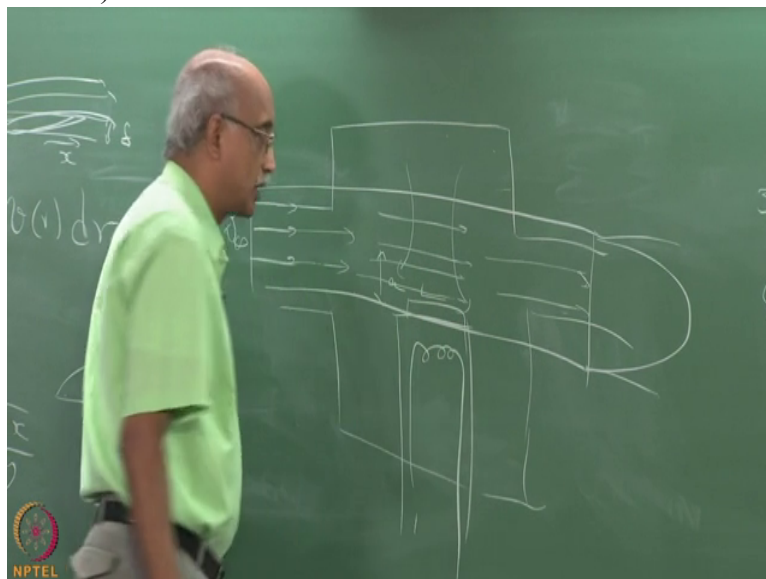
the substrate and only achieve laminar flow conditions downstream. Now is that the right strategy? I mean what is the, you know, if we do, if the flow happens this way what is the downside?

See the thing we have to remember is material is distributed in this direction, right? It is distributed among all the stream lines that are flowing. If the entire flow occurs in the plug flow, then only the bottom-most layer of the fluid will ever come in contact with the substrate. The rest of the material will just get...so that is not the right way to do it.

In fact the transition to an uniform flow which is still a mixed flow, you know, that is the key thing. You want to have a mixed flow condition before the fluid encounters the substrate but at the same time you do not want turbulent mixing. You essentially want a laminar mixing to occur. The problem with plug flow again is there is no interlayer transport through diffusion.

The difference between a simple plug flow and a parabolic laminar flow is that now there is mixing of the reacting species across the streamlines instead of simply being conveyed along the streamlines. So you do want the transition to happen upstream.

So is there a formula for that? I mean how do you calculate where that transition will happen? Have you come across any equations that talk about transition from plug flow to parabolic flow? Actually 0:34:56.0 derived an expression which is, continues to be used quite effectively. 0:35:03.5 equation says the transition distance, that is the downstream distance at which the transition from plug flow to parabolic flow happens can be written as a by 5 squared times the Reynolds number where a again is the radius of the tube.

(Refer Slide Time 35:33)
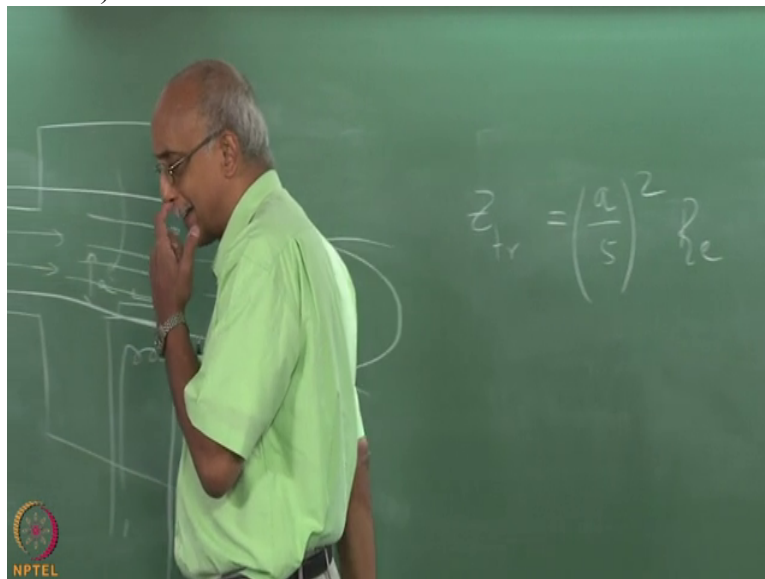
So what it basically means is that the Reynolds number, as the Reynolds number increases the transition distance also increases.

So that is another argument for keeping the Reynolds number as small as possible so that this transition will happen faster. As you can imagine, as the flow velocity is increased the Reynolds number increases the likelihood of never having the transition take place is higher. I

mean the fluid can just go past the plate in plug flow and then exit before you know what is happening. So by slowing down the flow lot of good things happen.

That is why in the C V D reactor, the whole intent is to keep the flow rate as low as possible. It helps us with managing the flow dynamics. It helps ensure that the transition from plug flow to uniform flow or parabolic flow will happen upstream of the substrate. It helps us ensure that there is no turbulence and all the, you know, non-uniformities and inconsistencies associated with turbulence. Thirdly it gives a chemically, the reacting species sufficient residence time inside the reactor to ensure that contacts happen and chemical reactions happen and equilibrium is achieved.

Chemical equilibrium is a time dependent phenomenon. So the longer that the chemical reaction has available to happen, the more likely it is that it will push itself towards equilibrium conditions. So by slowing down the flow you can achieve a lot in a C V D reactor, right and so again when you are designing the reactor this, this kind of correlations are very helpful in ensuring that you control the spacing between the inlet and the substrate in such a way that you ensure that the transition happens prior to the fluid encountering the substream.

So we have kind of touched a little bit on the thermodynamic side, touched a little bit on the transport side, so when you are trying to model a C V D reactor in terms of its transport and thermodynamic properties, essentially the way you would want to do that is using C F D, computational fluid dynamic programs for modeling a C V D reactor are available. In fact most of the commercial C F D packages will have a subroutine for C V D phenomena.

But the way that they do it, sometimes is not accurate. Because they do not take into account the two-way coupling between the chemical reactions and the transport phenomena. Essentially if you look at a conventional program for modeling a C V D reactor, it will first deal with the flow and let the flow establish your velocity conditions, your pressure distribution, your temperature distribution.

And then, the, it will then call upon some chemical kinetic code or equilibrium code to establish the corresponding species concentrations at each location inside the C V D reactor

and then based on these conditions it will calculate the rates of transport of the species to the substrate and then for example if silicon is what you are trying to deposit and silicon is distributed among 10 species, it will calculate the rate of deposition of each of these species and from that it will calculate an effective deposition rate of tungsten simply by as a weigh/weighted, as a weighted sum of the deposition rates of all species containing the element silicon. That is the conventional approach.

The problem with that approach is it may not be self-consistent because it is assuming that transport and chemic/chemical, and the thermodynamic processes can be decoupled. Its, for the most part, it is true. Particularly when the depositing species are in dilute amounts. If you are using a carrier gas and for example your silane is only present in trace quantities then one part of the assumption is true, that transport of that species is not going to affect the macroscopic flow characteristics of the system.

But if you are not using a diluant and you are feeding in the reacting species at reasonably high concentrations, concentrations that are not much less than 1, then even that assumption is not valid. Because the diffusional transport of the species can have an influence on the convective transport in the reactor. So there is something called Stefan flow which is, we will talk about a little later in this course which is the convective flow
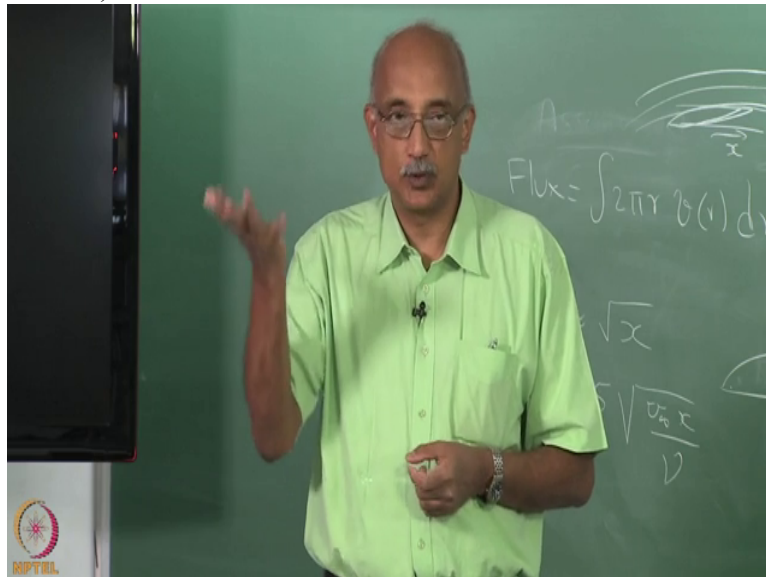
(Refer Slide Time 40:31)

which is induced by diffusive flow.

You know, according to mass conservation, if you have a diffusional flow from the bulk

of the fluid towards the substrate it must be opposed by something. So the diffusional flow induces an equal and opposing convective flow of the fluid which is called Stefan flow which can have a very significant influence on the flow dynamics in the system. That is a very important effect in a C V D reactor which is typically neglected in most of the commercial C F D codes that, that deal with C V D reactors.

The other aspect that again we deal with in much more detail later on is the self-consistency aspect. Let us say that you are trying to deposit silicon on a substrate, right. From a transport viewpoint, what is the primary constraint you have to impose on the system, to get a meaningful solution? The constraint is the flux of silicon must be positive towards the substrate, right? The flux of elemental silicon, not every species containing silicon.

So the silicon element is contained in the 50 species inside the C V D reactor, 40 of them or 25 of them could have a flux towards the substrate, 25 of them could have a flux away from the substrate. That is Ok as long as the net flux, when you add up the contributions of all the species are towards the substrate. That is the self-consistency check. If we have a C V D film which has more than 1 constituent, for example let us say that you are trying to deposit silicon nitride, S i 3 N 4, then what is the transport constraint that you should impose?

There are actually three now, the flux of silicon should be positive towards the substrate, the flux of nitrogen should be positive towards the substrate and in order to get the stoichometric condensate of S i 3 N 4 the molar fluxes of silicon and nitrogen must be in the ratio of 3 to 4 right, 3 by 4. So all of these constraints must be simultaneously applied in order to have a self-consistent solution. And again commercially available C F D codes won't even try to do that.
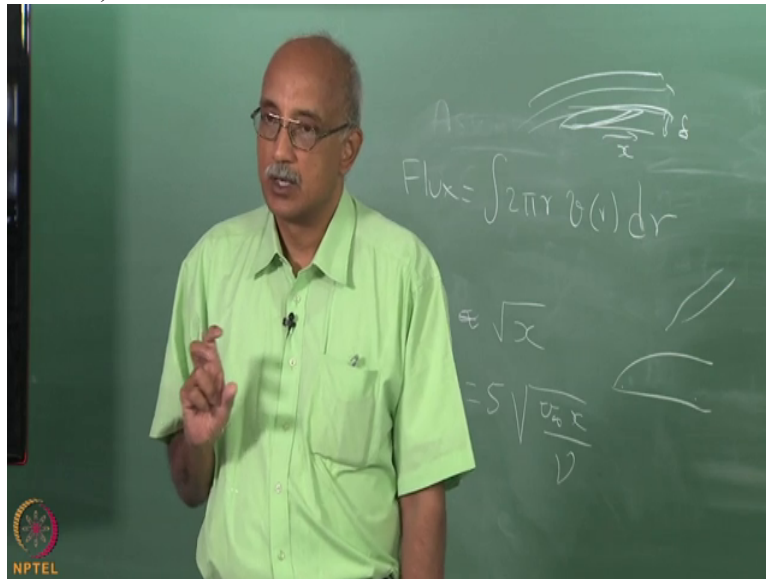
So these are some of the, the gaps in the current approach to modeling of C V D processes in commercial code. So what we will try and emphasize

(Refer Slide Time 42:56)
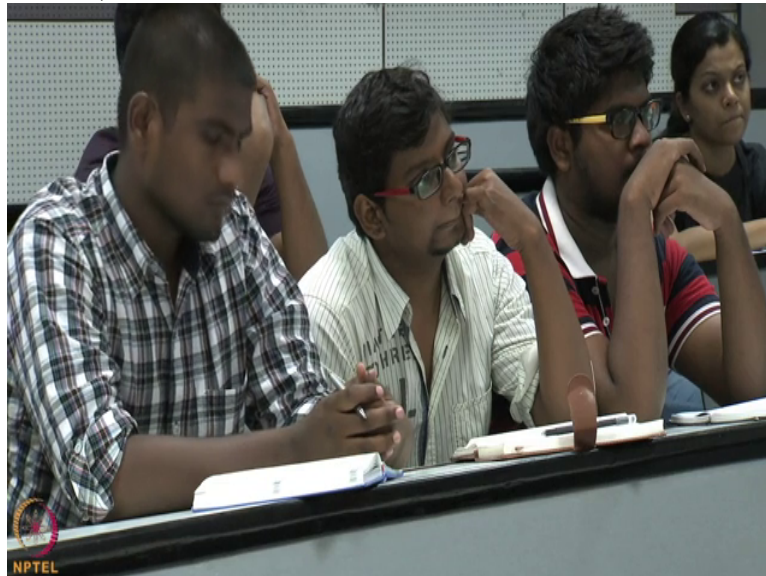
in this class is some of these, very interesting, interdependent effects.

(Refer Slide Time 43:02)

And the fact that you, you obtain the rate of deposition of the C V D film and even its dew point accurately only if you impose not only the thermodynamic and transport constraints that affect the so-called macroscopic environment of the C V D reactor but also the diffusional transport constraints that apply at the interface between the fluid and the substrate.

And that is where the iterative solution process becomes very important. Ok. So let us stop at this point and we will continue the discussion in the next class. Any questions on what we have covered so far? Ok, see you in the next class then.