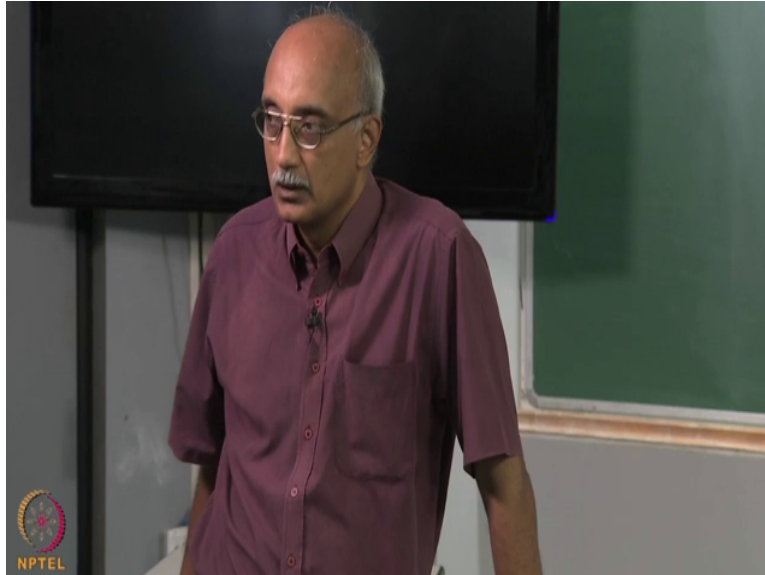


**Chemical Engineering Principle of C V D Processes**  
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**Indian Institute of Technology Madras**  
**Lecture No 03**  
**Overview of CVD Process Fundamentals**

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Good morning and welcome to the next lecture in our course on chemical engineering principles of C V D processes. So in this lecture we will continue to discuss some of the basics of the processes and equipment and in particular focus on the thermodynamics slash kinetics aspects as well as the transport phenomena. This lecture will be more of a, an introduction to these mechanisms in C V D reactor and we will deal with them in more detail in future lectures.

Ok now just to recap, C V D is a process that is used to make many kinds of useful thin films on surfaces. So the kinds of films that you can make, you can make metals, ceramics, semiconductors and various composites. Now the type of metals that are frequently deposited using C V D are tungsten is one, copper is another one, semiconductors of course silicon and germanium are the two that are most commonly deposited and they are used mostly in semiconductor microelectronics wafer fabrication, integrated circuits and so on.

As far as composites go, the most common kind of composites that you can use, make with C V D is metal ceramic composites. And these are typically efficiently deposited using C V D because all you really have to do is adjust the precursors by introducing the right mix of

vapor species into the C V D reactors you can make either pure metal films or you can make pure ceramics films or composites of these or semiconductors or insulators or conductors whatever you want.

So the process itself pretty much lends itself to the deposition of any kind of film that you want. C V D can also be used to make very fine fibers. So these could be optical fibers for various purposes. Even some of the, the carbon nanotubes are used, are made using C V D processes. It is again a way to make nano-sized materials as well essentially by using the C V D processes initial step to make Angstrom sized materials and then growing them to make nano-sized particles.

So we mentioned in one of the previous lectures that a C V D reactor can actually be turned into a nanoparticle synthesis reactor by providing conditions so that there is homogeneous nucleation of very fine particles. On the other hand, C V D reactor can also be used to make nano-sized materials on a substrate simply by allowing the C V D film to form initially but not as a continuous film but rather as clusters of particles which then coalesce to form larger particles. So you can also do nanoparticle synthesis on surfaces using C V D reactors.

And so in the C V D process, while most of the time you are trying to make continuous films on surfaces, sometimes we try to make powders as well. Powders are essentially isolated regions where you have agglomeration of, of particulate material and these you can use for various purposes.

So given the fact that C V D is a very flexible technology to make various types of surface products it is important to understand what type of equipment you need to make what type of C V D product. And also what precursors should you use again in order to achieve the C V D material that you are looking for.

So in terms of precursors, essentially the, the three most popular types of precursors are hydrides, for example S i H 4, silane as silicon tetra hydride, the second one is halides S i C l 4, S i H 2 C l 2 are examples of those. And the third one is metal organics. These are various organic compounds of various metals and semiconductors and so on.

Now the reason that these are in particular preferred as precursors for CVD is that they combine two properties. One is they are very reactive. Obviously in a CVD reactor, you want the species to be ready to react as soon as they enter the reactor. But at the same time, they should be stable enough so that they do not decompose by the time they are fed into the reactor.

So in the supply system itself you want them to remain in their basic form. When you are feeding reactants into the CVD reactor as I mentioned earlier, you really do not want to mix the reactants. You want to keep them separate. But even so, if the reactant is extremely reactive, it can actually dissociate or start reacting with the pumping material and so on.

So you need precursors which are reactive enough but not too reactive. Those are the best kinds of reactants to use and these compounds kind of fulfill both criteria. So, for example if you want to make a pure metal, then you may want to go with fairly simple hydride molecule or a metal organic molecule as a precursor.

On the other hand if you are trying to make compounds, then you probably want a mixture of at least 2 species, one of which contains one element in the compound and the other which contains the other element in the compound. And during the reaction, they deposit a film which is then a compound of both the elements.

So for example you could have carbon which is embedded into a tungsten carbide material. So essentially carburizing, nitriding are all done in this fashion. And even formation of oxides, for example if you are trying to form titanium oxide as a film, then you typically will introduce titanium as a reactant to, let us say TiCl<sub>4</sub>, and the oxygen will then come in through an oxidizing species which could be again an organic compound which has oxygen present in it.

And during the reaction, the Ti and O will find each other and they pass out as a TiO<sub>2</sub> film. So these are you know, some ways you can look at CVD reactors, you know, based on what type of product you want to make.

For example if you are trying to make a coating on a surface, coatings have certain characteristics requirements. They must be extremely well-adhered to the substrate. They must have very fine grain structure. Obviously they must be chemically stable. They must be able to withstand aggressive conditions of temperature, humidity and also they must be impervious to mechanisms like corrosion and erosion and so on. So they, they must satisfy these criteria and yet they must be very thin. So the challenge is to make a very thin film on a surface which can still satisfy all the functional requirements that the coating has to satisfy.

And that is one reason why C V D is a very popular process for depositing coatings on surfaces because it is able to satisfy all these conditions simultaneously. Now another way to look at C V D reactors is in terms of the operating conditions. Is it a high temperature reactor or room temperature reactor? Is it high pressure reactor a low pressure reactor?

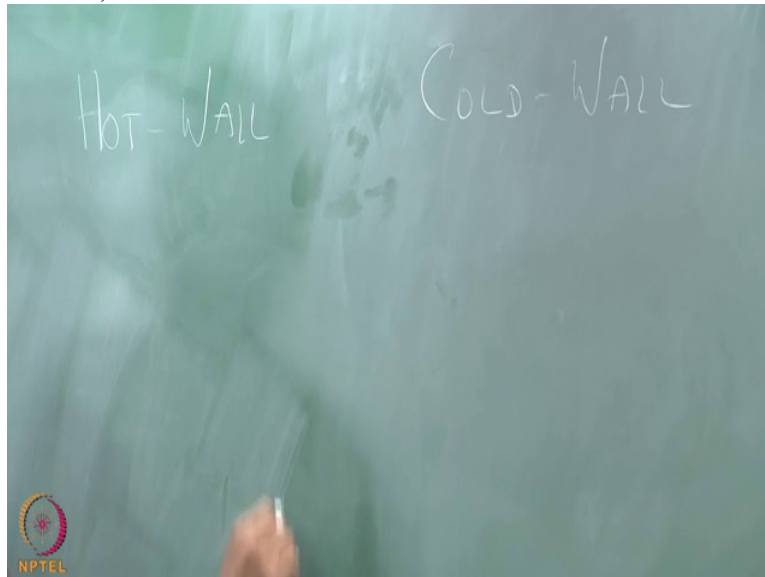
Now there are reasons again that dictate your decision as to whether you design it one way or the other. Now typically a high temperature reactor is chosen when you want a film which is more crystalline in its structure. Whereas temperature that is closer to room temperature can be employed when you do not care so much about the crystallinity of the structure but you care about, for example not changing the properties of the substrate itself.

And so obviously, higher the temperature that you operate the substrate at, the greater will be the rate of deposition. So as you lower the temperature closer to room temperature, the rate of deposition will decrease as well. So again if you are trying to make thick films you want to operate in the high temperature region where as if you want to make a very thin film, you are probably better off operating in the low temperature region.

Pressure also plays an interesting role and actually the combination of temperature and pressure is very interesting in order to achieve certain characteristics in the reactor. Now in terms of the temperature of the reactor, there are really again, two modes in which the reactor can be operated. One is known as a hot wall reactor and the other is known as the cold wall reactor.

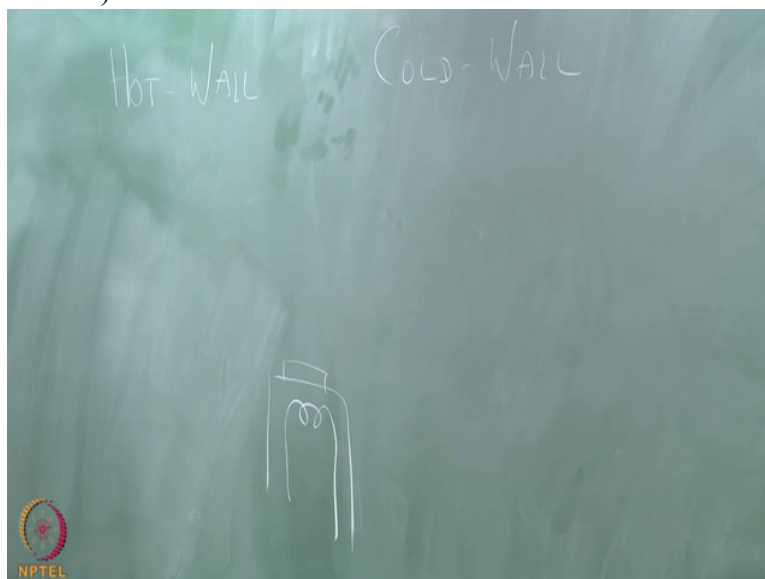
Now the difference between these two is

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you know you have the substrate which is being provided with an external energy source on which

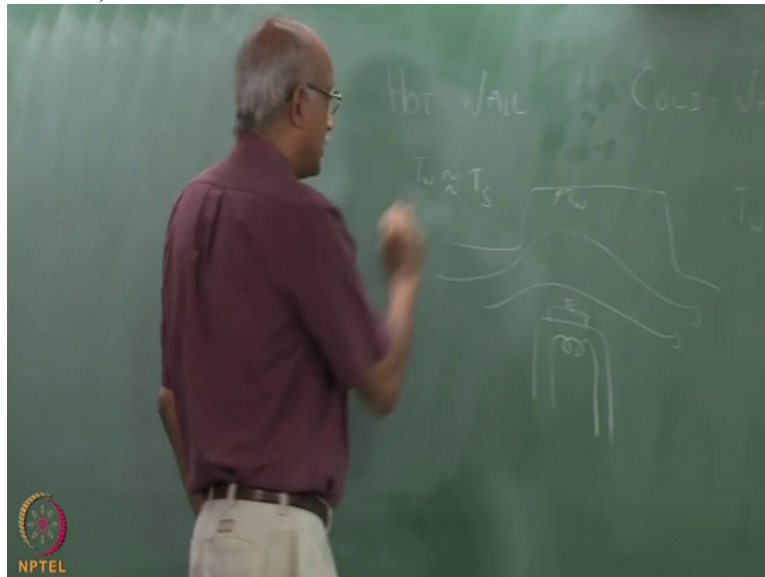
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you are depositing the film and you have the reactor and gases flowing through the reactor. Now if the substrate temperature is some, let us say  $T_s$  and let us say the walls of the reactor are at some temperature  $T_w$ , in the case of the hot wall reactor,  $T_w$  is approximately equal to  $T_s$ . And in the case of cold walled reactor,  $T_w$  is much smaller than  $T_s$ .

Now when you look at these two cases, what are the advantages and disadvantages that you can think of?

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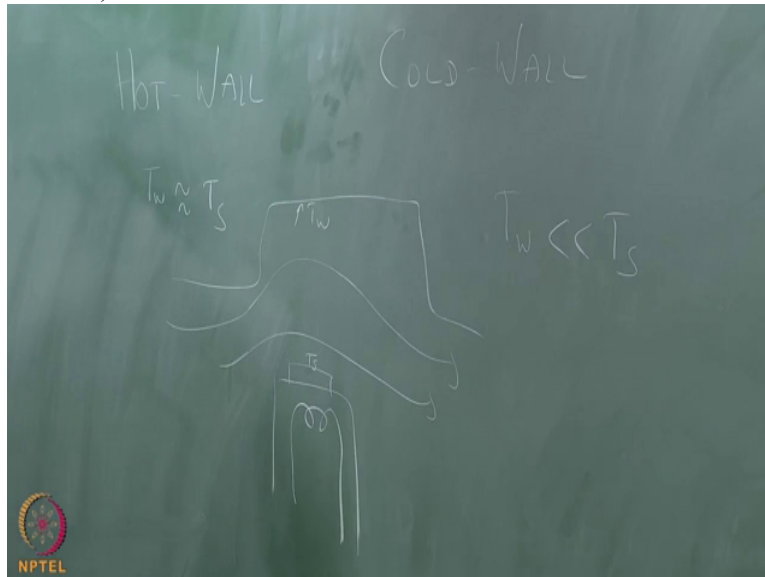


When the wall temperature is approximately equal to the substrate temperature, essentially what that means is you are not heating the substrate too much. Because you expect that the reactor itself will be kept fairly close to room temperature so when say the difference in temperatures is small, what we are talking about is that the substrate is not being heated to a very high temperature.

Now what is the biggest benefit to doing it this way? Well first thing, there is energy conservation, right? The hotter you have to heat, the more energy we have to supply. So if we can make the process run at a lower temperature, you should always be happy. What is the other advantage that, that you can think of? Well it turns out that in a CVD reactor one of the things you have to watch out for is the flow dynamics. How is the material being convected into the reactor and how is it being allowed to diffuse to the substrate to allow for film condensation to happen.

When you have a case where  $T_s$  is much greater than  $T_w$ . In other words

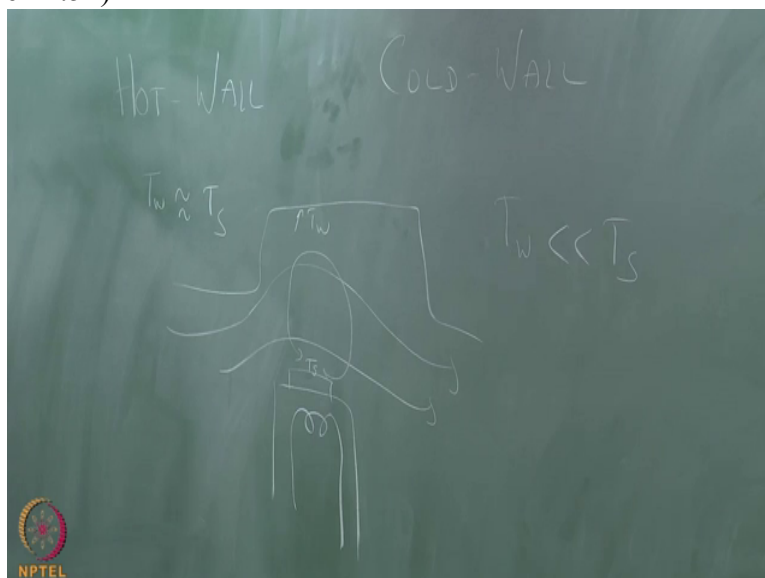
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the hot wall case, what happens from the flow dynamics viewpoint, what do you expect will happen? Do you think that will have an influence on how flow happens? So there will be a big density gradient, right? The gas that is closest to the substrate is much lighter than the gas that is far away. So essentially what would happen?

When  $T_w$  is much smaller than  $T_s$  you will start getting these recirculation loops in the system

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and as I was mentioning in the last class that is something you do not want to have. You want flow in a CVD reactor to be unidirectional and laminar as far as possible. You do not want

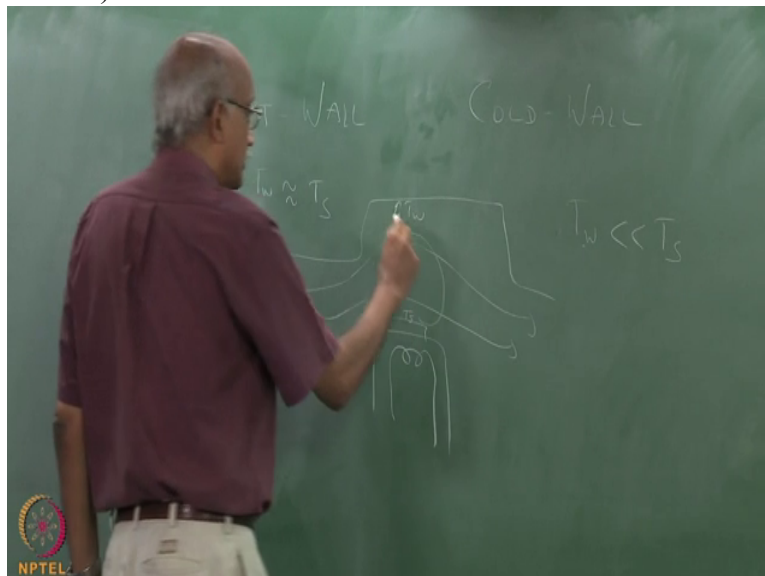
these convection cells or recirculation zones to be set up within the reactor because that can lead to unpredictable deposition behavior.

You may get very thick deposits in certain locations and virtually no deposit in other locations. So clearly, you cannot avoid it. It is a natural convection, right? So anytime there is a temperature gradient you are going to set up a natural convection flow. But what is the, so that is the main disadvantage of a cold wall reactor where the substrate is being maintained at a much higher temperature. But what is the advantage of a cold wall reactor? Why would you want to do that?

The main reason you want the cold wall reactor is so that you make sure that the nucleation only happens in a heterogeneous fashion because only the substrate is at a high enough temperature to actually promote deposition to happen. And you essentially preclude homogenous nucleation from happening.

Because in this configuration, the,

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all the rest of the reactor is at a much lower temperature. So thermodynamically and kinetically the formation of condensed phases is not favored. In the cold wall reactor you can pretty much rest assure that you do not have to worry about the formation of the condensed phase in the bulk gas and then the transport of these particles to the substrate which can obviously degrade the quality of the film.

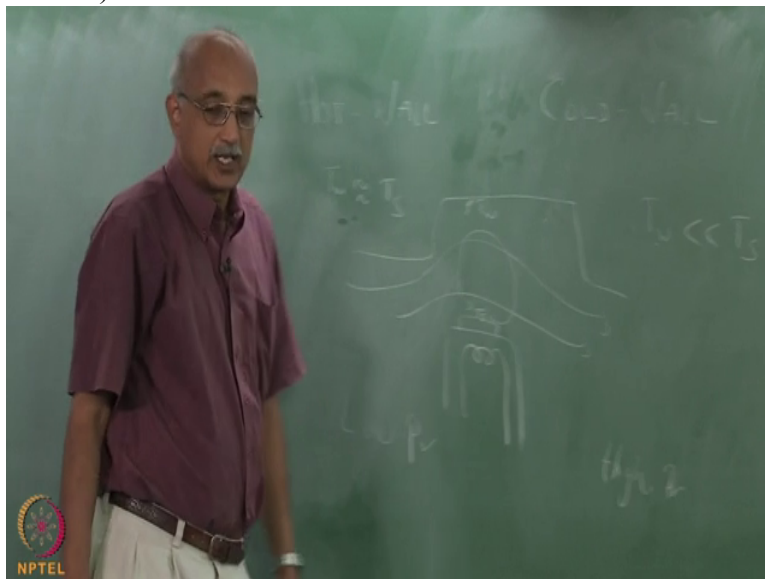


But in the case of the hot wall reactor, although you are avoiding this natural convection flow due to a steep temperature gradient, you now have to deal with the possibility that you could have a lot of nucleation of the condensed phase in the gas itself. So you may get a lot of loss of material which may be actually depositing on the walls of the chamber and even worse, occasionally the material that is depositing on the walls of the reaction chamber will flake off and drop on the substrate. So instead of getting a nice smooth film, you will have very powdery and flaky deposit on the substrate.

So there are clearly pros and cons to both configurations. So you have to have a reasonably good idea in your mind as to which way you want to go.

Now how does pressure play into this? When does low pressure help and when does high pressure help?

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Well, again pros and cons. When you are, as I mentioned the other day when I say high pressure in a C V D context we are really talking about atmospheric pressure, right?

Now under atmospheric pressure conditions again, chemical reactions will run much faster. They are more likely to reach equilibrium because both pressure and temperature are typically accelerators for chemical reactions. So you can expect that when you have a pressurized chamber or at least atmospheric pressure chamber the probability that two molecules will find each other and react is much higher.

The reason is that, at higher pressures the molecules are squeezed closer together so they are more likely to react. In other words, their mean free path is going to be much smaller than the dimensions of the chamber. So the collisions between molecules are very likely.

At lower pressures what can happen is the mean free path can expand sufficiently that it actually becomes comparable with the dimensions of the chamber itself, which means that it is possible that two molecules may never find each other. So lower the pressure that you operate at, the less intense the reaction becomes.

What is the positive part of operating at low pressure then? Well, for one thing, you can certainly affect the structure of the film. For example if you are trying to make an amorphous film or a polycrystalline film you are better off using low pressures because, you know, you do not really want a very structured film to form. And also if you are only looking for low deposition rates and very, very thin films low pressure is better because at high pressure, you know the deposition rates become quite large.

On the other hand although high pressure promotes chemical reactions, it does slow down the diffusion process, right? Whereas at low pressure even though chemical reaction is slowed down, diffusional processes speed up. So you really have to analyze your particular reactor to understand what is the rate limiting mechanism and make sure that you design the reactor so that you remove the bottleneck wherever it is.

For example if your C V D system is transport constrained, then you probably want to operate at low pressures so that you speed the diffusion process. On the other hand if your C V D process is kinetically constrained then you want to operate at high pressure so that you can make the kinetics run faster.

The other effect that pressure has is actually affecting the flow itself within the chamber. It turns out that these convection cells or recirculation loops that I talked about are significantly reduced when you lower the pressure. Their effect is much greater as pressure increases.

So if you want to run a reactor that is a cold wall reactor but you do not want to deal with the problem of free circulation, then you are better off using lower pressures because they have the effect of essentially collapsing these convection cells and making the flow very uniform. So a lot of, you know, complex interplay that you need to think about when you are designing a C V D reactor. Now in terms of chemical analysis one of the first assumptions we make when we talked about the C V D reactors is that the flow is laminar, as I said. And also the velocity of flow is low enough that the molecules have plenty of time to find each other and react.

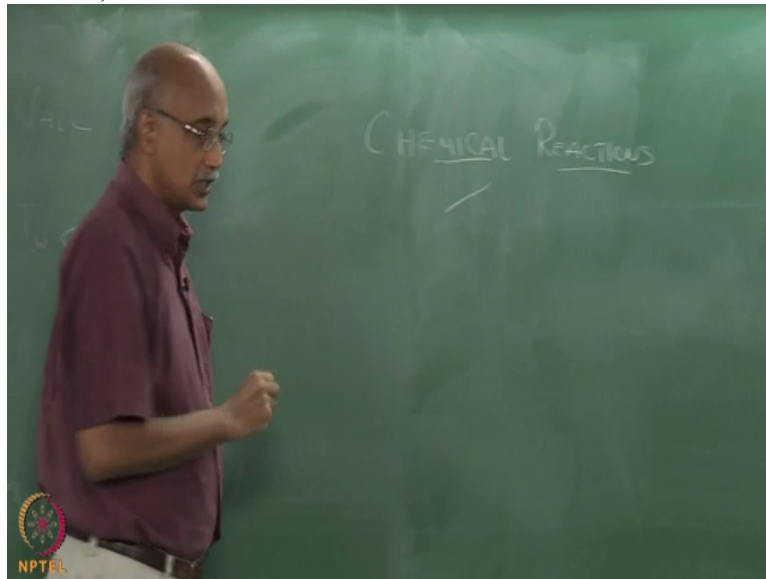
So what that means is that by the time the reactants enter the reactor and to the time they exit the reactor, there is sufficient residence time of the reacting species inside the reactor, for them to reach chemical equilibrium so you can essentially assume that all chemical reactions reach equilibrium which means that for characterizing any reaction between species to form a product, you can assume equilibrium rate constants and do your calculations based on that.

So that is one limiting case obviously of looking at the chemical reactions inside the C V D reactor where as we were just discussing it is a valid approach when you know that conditions inside the reactor are approaching equilibrium conditions.

What that requires, a, low rate must be slow enough that there is plenty of time for equilibrium to happen in the reactor and b, the pressure in the reactor must be high enough that the molecules again get pushed against each other and react. So under high pressure, low flow conditions the chemical equilibrium assumption is quite valid.

Conversely, of course as the flow rates increase and or the pressure decreases, you have to start questioning the assumption of chemical equilibrium and you have to start introducing chemical kinetic factors. So if I were to do an analysis of chemical reactions in a C V D reactor, the two extreme cases

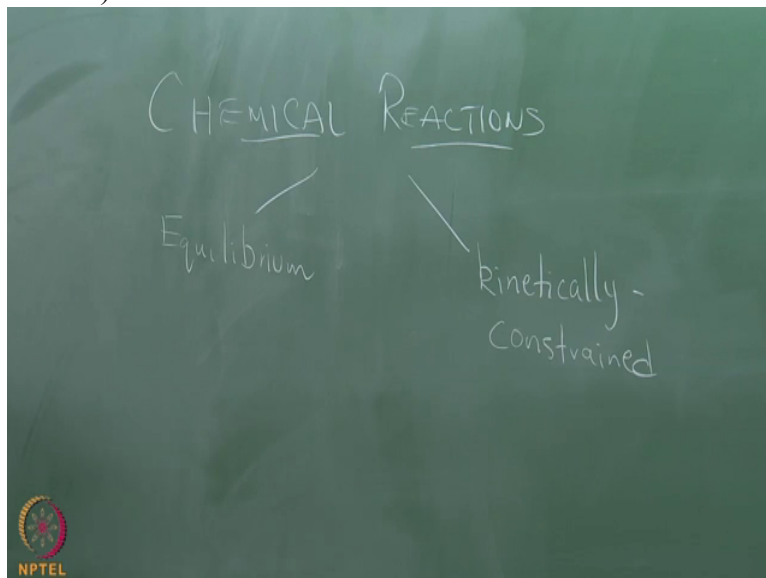
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that I can look at are one, where equilibrium prevails and the other where you have a kinetic constraint.

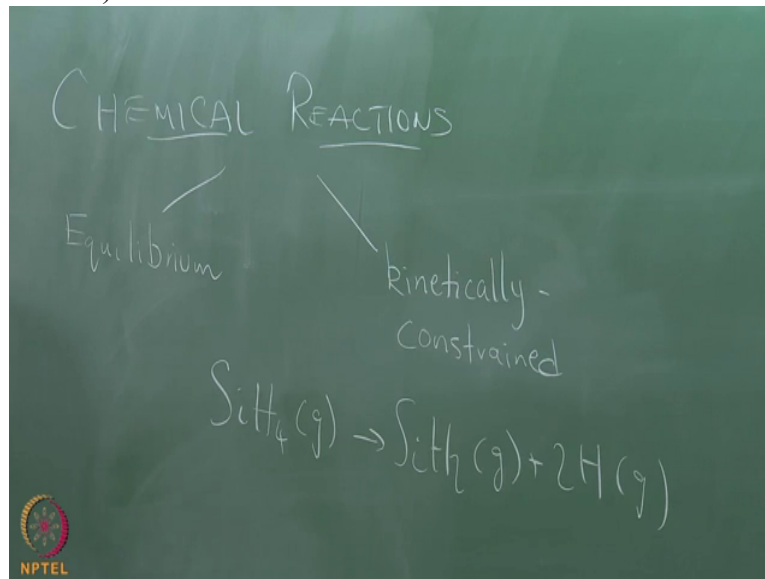
So what that means is

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if I look at a very simple reaction inside this CVD reactor where let us say,  $\text{SiH}_4$  gas goes to  $\text{SiH}_2$  gas plus  $2\text{H}$  which is a typical

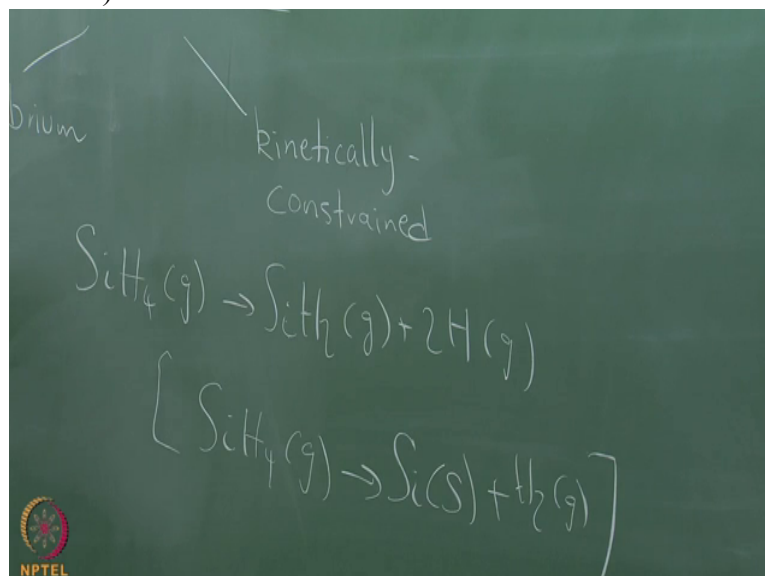
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gas phase reaction that would happen in a, you know, pyrolysis CVD reactor where  $\text{SiH}_4$  is getting broken down into  $\text{SiH}_2$  plus  $2\text{H}_2$ .

So this is only one process step in the overall reaction which is  $\text{SiH}_4$  gas going to  $\text{Si}$  solid plus  $\text{H}_2$  gas which is the pyrolysis reaction I mentioned in the first

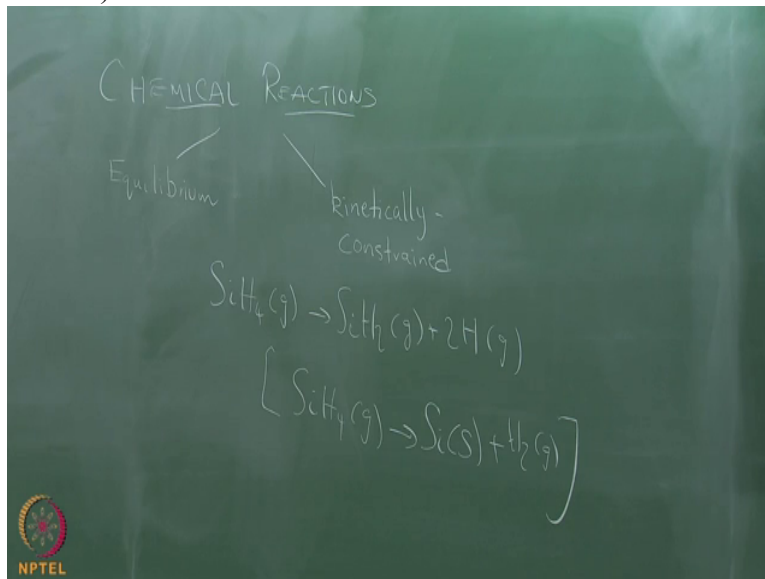
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or second lecture. But to go to the step, obviously it is not going to go in one step, right, there is going to be a lot, many, many gas phase reactions that happen and finally the depositing species are going to get transported to the surface and then the film formation is actually going to happen.

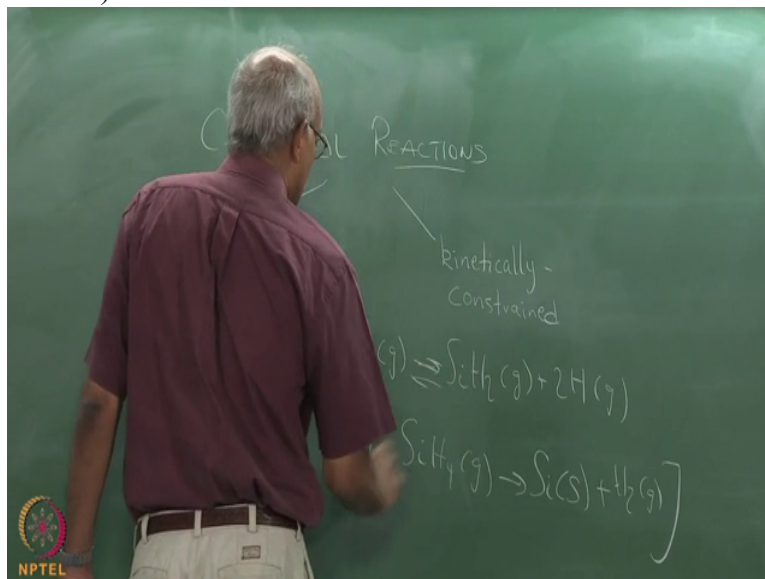
So if I just look at one step here, the

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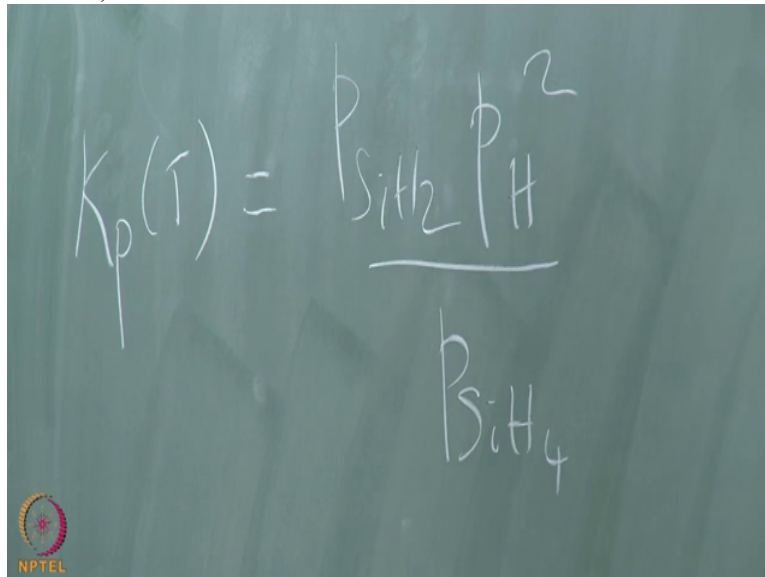
SiH<sub>4</sub> gas going to SiH<sub>2</sub> plus 2H, you can certainly write this equation in terms of, you know this is let us say reversible reaction,

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so you can write some  $k_p$ , it is a function of temperature equals  $p_{\text{SiH}_2} p_{\text{H}}^2$  over  $p_{\text{SiH}_4}$  where this  $k_p$  you can write it as some

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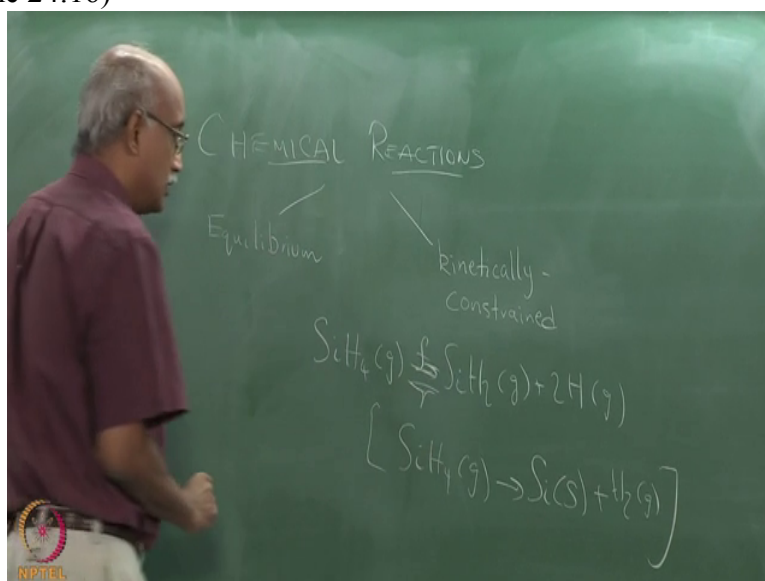


$k_p$  zero exponential minus  $\Delta T$  by  $k T$ . So you can actually calculate rate constant from the thermodynamic properties of the reacting species.

So if  $k_p$  is known at the temperature that the reactor is running at, then you can actually solve for the reacting species by doing a mass balance in the, in the reactor. But this is, of course assuming that chemical equilibrium is prevailing.

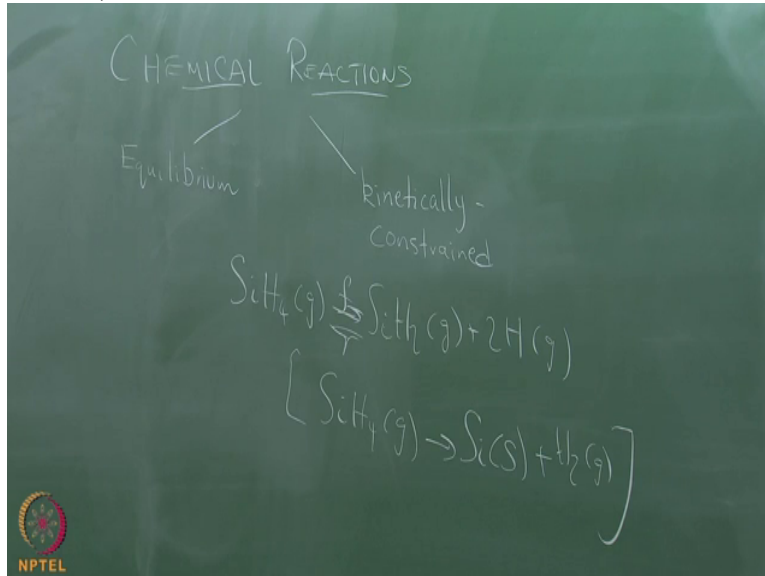
But the other extreme of this, as I mentioned earlier is kinetically limited. So let us say that this is the forward reaction and this is the

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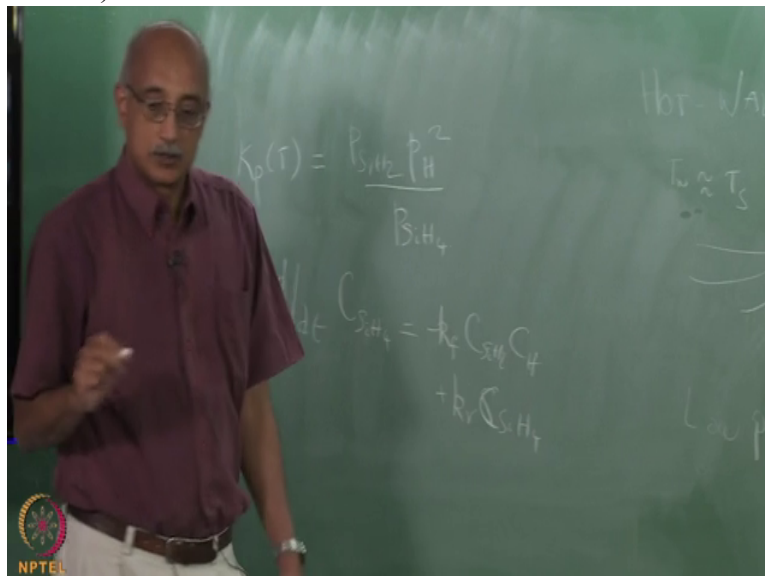
reverse reaction, then in the case where reaction is kinetically limited you have to write it as  $\frac{d[\text{SiH}_4]}{dt}$  equals

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$k_f$  minus  $k_r$  times concentration of  $\text{SiH}_2$  concentration of hydrogen plus  $k_r$  times concentration of, so I have to write it

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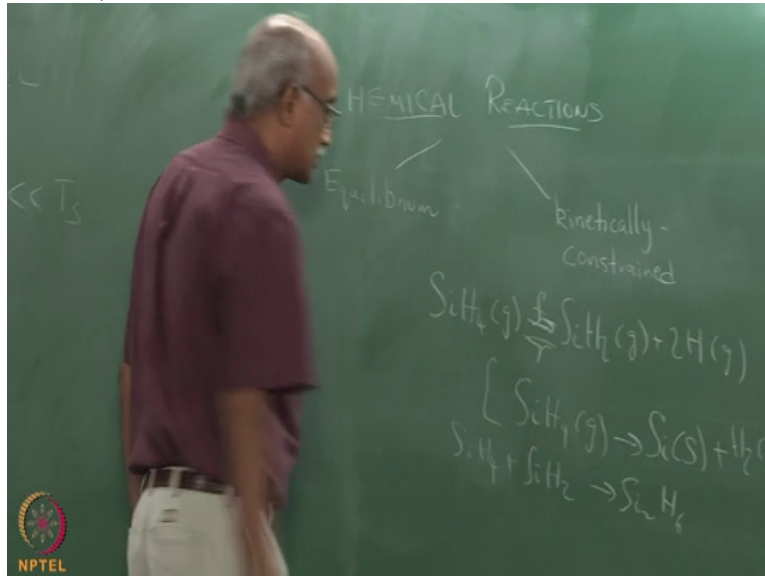


as rate equation, right, and we have to look at how the concentration changes for a given combination of  $k_f$  and  $k_r$ . Now this is just looking at one reaction.

But then in the actual system this is not going to be the only reaction, right? For example this  $\text{SiH}_4$  may react with the  $\text{SiH}_2$  to form  $\text{Si}_2\text{H}_6$ . So that could be the next step if that happens in the gas phase. And the next reaction would be that this



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$\text{Si}_2\text{H}_6$  breaks up into  $\text{SiH}_2$  plus  $2\text{H}_2$ . So there could be literally dozens or even hundreds of these chemical reactions that are constantly going on.

Even in the equilibrium case, even if you can assume that equilibrium exists, how do you handle all that? You know there is going to be simultaneously a hundred reactions that are going on and rate constants that are involved, and it gets even more complex in the kinetically limited case to do this evaluation because you have to solve these equations simultaneously with your momentum transport, momentum conservation and energy conservation equation so that you know what is the local prevailing velocity, the local temperature and so on in order to be able to do these calculations.

And so, dealing with the reactant, the gas phase reaction part of it, even in the case where you can assume chemical equilibrium is challenging. So instead of specifying certain reactions and assuming reactions take place along a reaction path, there is another approach that can be used to calculate equilibrium compositions. Anybody aware of the alternative method of calculating equilibrium compositions without having to specify reactions?

What is, what is characteristic of an equilibrium state from a thermodynamic viewpoint?

(Professor – student conversation starts)

Student: Gibbs free energy

Professor: Free energy is minimized, right?

(Professor – student conversation ends)

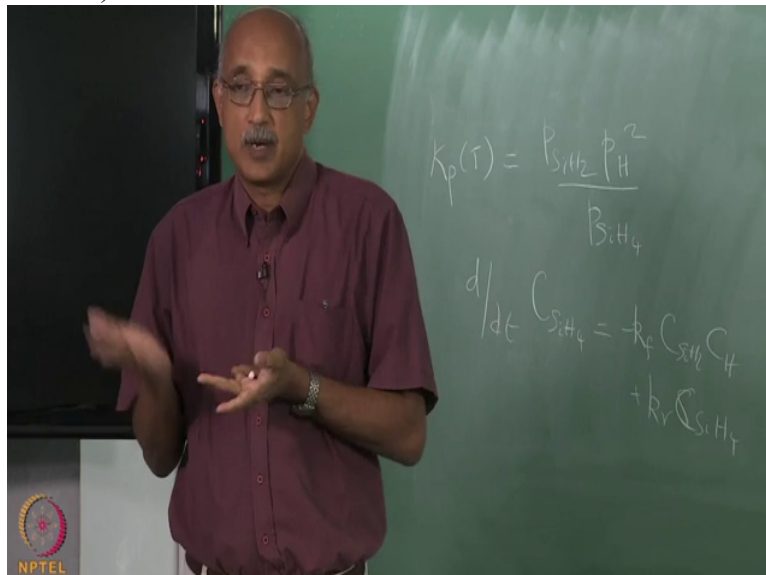
So in essence if

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you have an algorithm by which you can look at various combinations of products and calculate the free energy corresponding to each combination,

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then mathematically analyze it to see which particular combination of product species will give you the minimum in free energy; that should give you the equilibrium composition, right? And in fact that is the approach that is used to calculate equilibrium compositions in C V D systems. It is based on free energy minimization.

It is a very elegant method in the sense that you do not have to specify any reaction pathways. You do not have to say that, you know these are the 20 reactions that are going on, because you do not know. You are only guessing. Whereas free energy minimization has the huge advantage that you do not need to know anything about the reactions that transform the reactants into the products. All you need to know is what are the reactants and you need to know all possible products; that you do need. Which means that you need to have very extensive thermodynamic database that contains the necessary properties of all possible product species.

But as soon as you have that, it is a fairly simple mathematical exercise to, to do this. We will cover this in more detail in one of the future lectures because it is a very key thing to, to especially modeling CVD reactors and the formation of products in CVD reactors.

Now all that we have discussed so far are reactions happening in the gas phase. And even though they are quite complicated, they are actually quite simple when you compare them to the reactions that are going to be taking place on the surface. Because even less is known about heterogeneous chemical reactions when you have such a multiplicity of gas phase species that are coming in contact with the energized substrate.

For example the silicon that is actually depositing as a film on the surface may be getting delivered to the surface in the form of many different species. It could be coming in as  $\text{SiH}_4$ ,  $\text{SiH}_2$ ,  $\text{Si}_2\text{H}_4$  whatever. The thing what differentiates these species is what is known as the sticking coefficient. What is the probability that the silane molecule, that approaches a substrate will actually stick to the substrate rather than rebounding compared to, let us say,  $\text{SiH}_2$  molecule that is approaching the same surface.

For example it turns out that the sticking coefficient of  $\text{SiH}_2$  silylene is close to 1. As soon as a silylene molecule hits a surface it sticks. Whereas for silane the sticking coefficient is much smaller, it is about  $10^{-6}$ . Why do you think that is? I mean what do you think determines the sticking probability of a molecule on a surface?

A simple way to think about it is an inert molecule will have a much lower sticking probability than a reactive molecule. It just so happens that silane  $\text{SiH}_4$  compared to

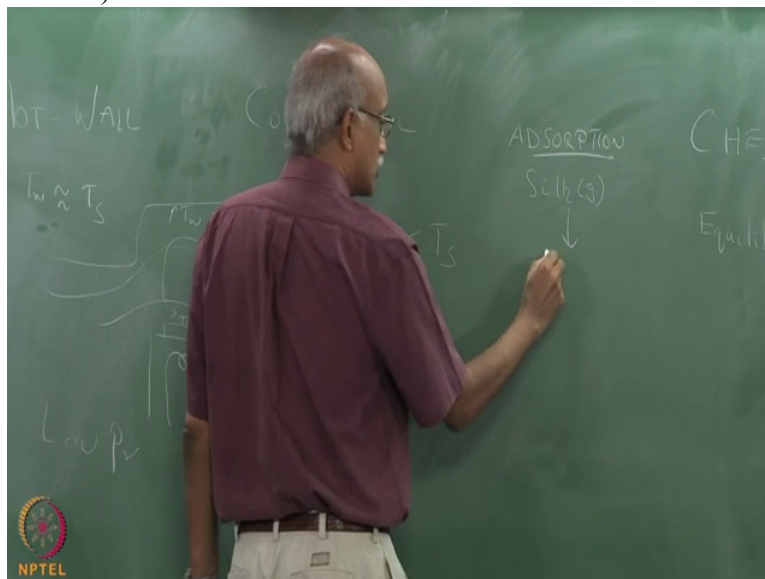
silylene  $\text{SiH}_2$  is much more stable molecule. So it does not immediately react whereas  $\text{SiH}_4$  is just ready to react as soon as it encounters the surface.

So what that means is that even though the concentration of  $\text{SiH}_2$  species may be much lower in the gas phase compared to the concentration of  $\text{SiH}_4$  species, the arrival rate or the deposition rate is actually the product of the flux of the species multiplied by the sticking coefficient or the accommodation coefficient. So when you look at it that way both silylene and silane contribute equal amounts of silicon to the surface. Because silane has a much higher concentration but lower sticking coefficient whereas silylene has a much lower concentration but has a higher sticking coefficient.

So it is really the product between the two that you have to keep in mind when you are trying to figure out which of the gas phase species is contributing the most to deposition occurring on the surface. But that is only the second step, you know. The first step is the formation of gas phase molecules. The second phase is actually delivering the molecule to the surface.

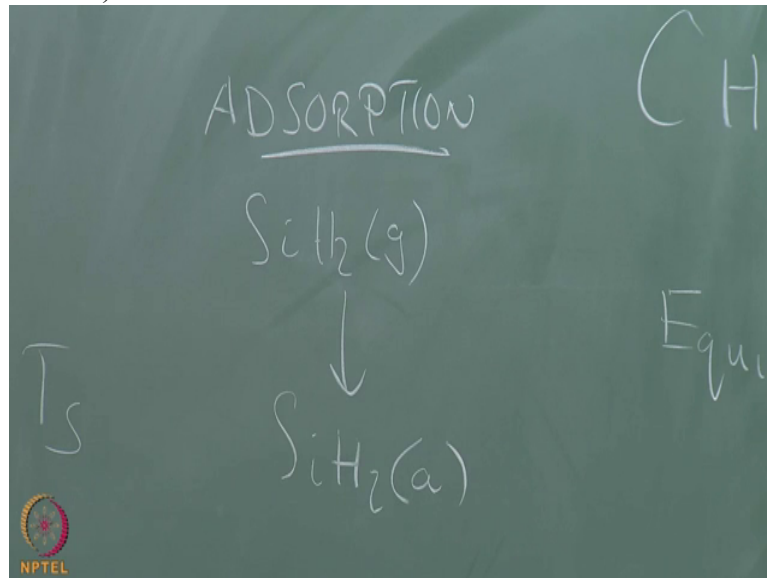
The third step is the molecule that has been delivered to the surface must get adsorbed on the surface. So for example, the adsorption step would imply that if  $\text{SiH}_4$  is getting delivered in the form of  $\text{SiH}_2$  gas

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to the surface, it must first become  $\text{SiH}_2$  adsorbed. The silane,

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silane molecule that gets delivered to the surface must first become attached to the surface through an adsorption process and here is where the sticking coefficient becomes very important. In the case of silane you can assume that virtually every molecule of  $\text{SiH}_2$  gas that comes to the surface gets converted to  $\text{SiH}_2$  adsorbed.

Now, but that is not the final process, right because now you have to get rid of the  $\text{H}_2$ . So there is also a desorption step involved. Now in order for desorption to happen, first this  $\text{SiH}_2$  molecule that has become adsorbed on the surface has to migrate on the surface until it finds the vacancy in which the  $\text{Si}$  can be accommodated. So it has to be able to move around the surface freely. So surface mobility becomes a critical issue.

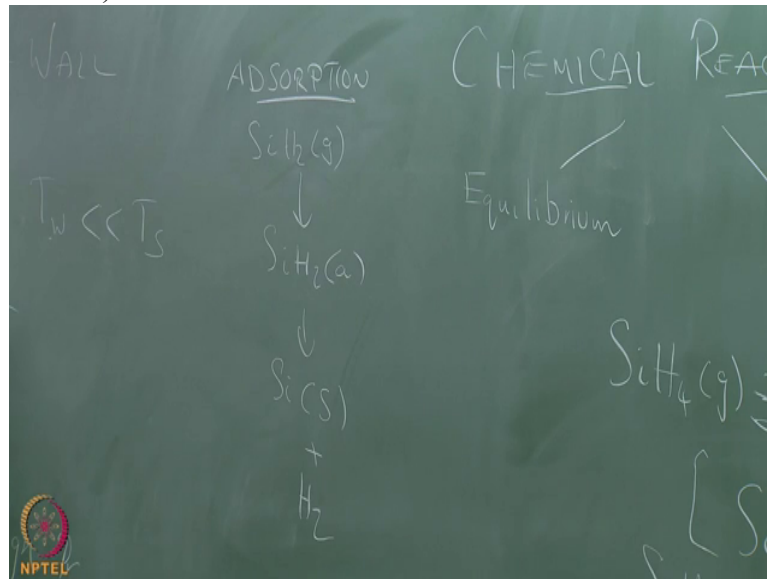
It is the diffusion of the adsorbed vapor on the surface that is a very critical step in ensuring a, the uniformity of the film and b, the formation of the film. And typically surface diffusivity is affected to a great extent by temperature. Unlike gas phase diffusivity, if you remember Fick diffusion coefficient and its dependence on temperature, it is only about  $T$  to the power 1 point 5 or 1 point 6. So it is not terribly temperature dependent.

However surface mobility has essentially an exponential dependence on temperature. So an increase in the temperature of the substrate has a tremendous influence on the ability of adsorbed molecules to move around on the surface which is why again high temperature operation is advantageous. It not only results in a high rate of deposition, it would also result

in a much more uniform film because the molecules are able to transport themselves around the surface much more easily.

So the next step from  $\text{SiH}_2$  adsorbed is for silicon to become a solid phase and release the  $\text{H}_2$  as a desorbed vapor.

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So that is the next step. And desorption also is a process that is enhanced by temperature. So temperature not only makes it easier for  $\text{SiH}_2$  molecule to move around and find the vacancy and therefore lose the silicon but it also makes it easier to dissolve the hydrogen and get it out of the system.

So those are all reasons why you want to keep the substrate as high as possible. It makes for a much thicker film and a much more uniform film. So if you are trying to minimize your cycle time and improve particularly the uniformity of your film, then you are much better off using a cold wall set up compared to a hot wall set up.

So this is basically what is going on, right, from a thermodynamic or a chemical kinetic viewpoint, the critical steps are a, the formation of the vapor phase precursors, b, is the transport of vapor phase precursors containing the depositing elements to the surface. Step 3 is the adsorption of the film components on to the surface; d, is mobility of adsorbed molecules in order to find a vacancy on the surface and step e is desorption of the excess

chemical in order to deposit the pure element or metal on the surface. It is essentially a 5-step process just from a purely thermodynamic viewpoint.

Now what you have to do is obviously combine this with the transport considerations in order to complete the description. Suppose you are running the C V D process and you want to know whether the process is transport limited or kinetically limited. How do you do that? What is the simple test you could do, any idea? 0:36:31.6

(Professor – student conversation starts)

Student: 0:36:31.8

Professor: No, no (laugh). Give me something specific. What conditions, what experiments,

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what is the critical parameter you would try to alter and, Ok and what would you measure?

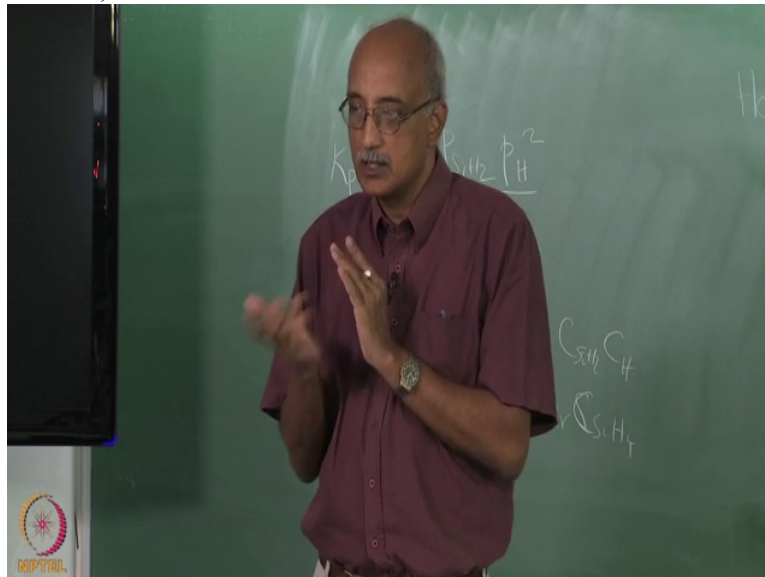
Student: 0:36:51.4 outlet

Professor: Outlet concentration of what?

Student: 0:36:57.7

Professor: Ok, much more direct test would be to

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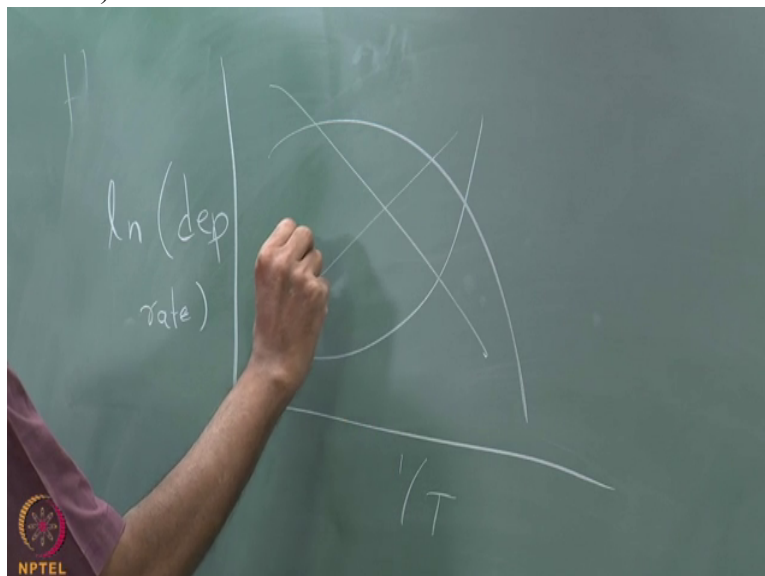
vary the temperature and look at the rate of deposition of the film, right?

(Professor – student conversation ends)

Much more functionally relevant also because that is ultimately what you care about. So suppose you take, suppose you do that experiment and you plot  $1/T$  versus logarithm of the deposition rate in a CVD reactor in which higher temperature is more favorable to the formation of a deposit, how do you think this curve will look, any idea?

Will it look like this, will it look like this, like this, like this, like this. Let us say this is

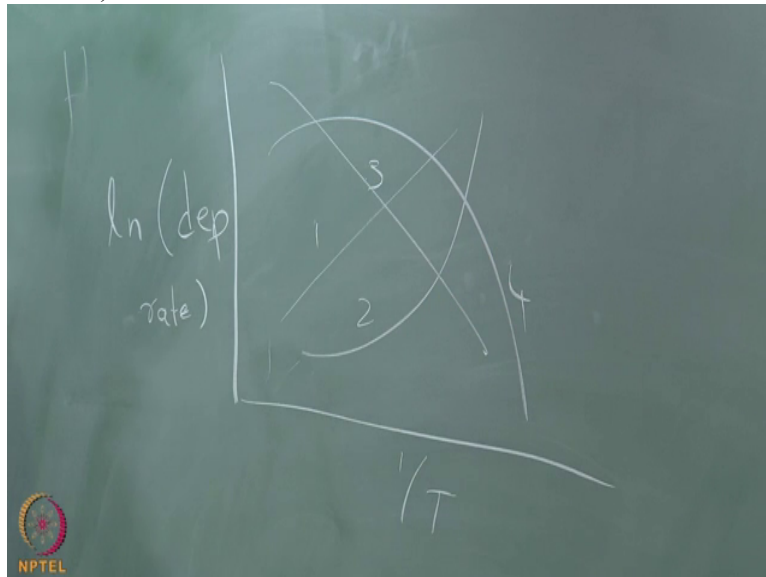
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1, 2, 3, 4.



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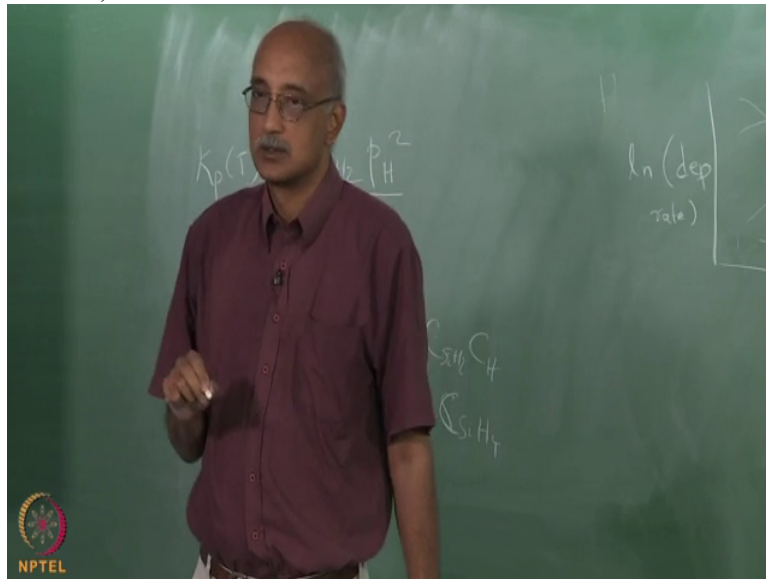
How many vote for 1? 2? 3?

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3 is quite this, straight line?

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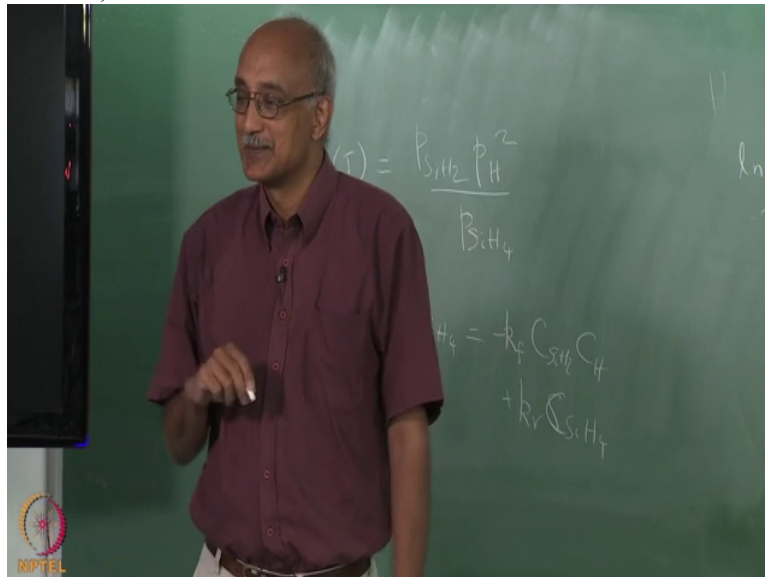
4?

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1 and others have absolutely no opinion. You do not think it is going to like any of these?

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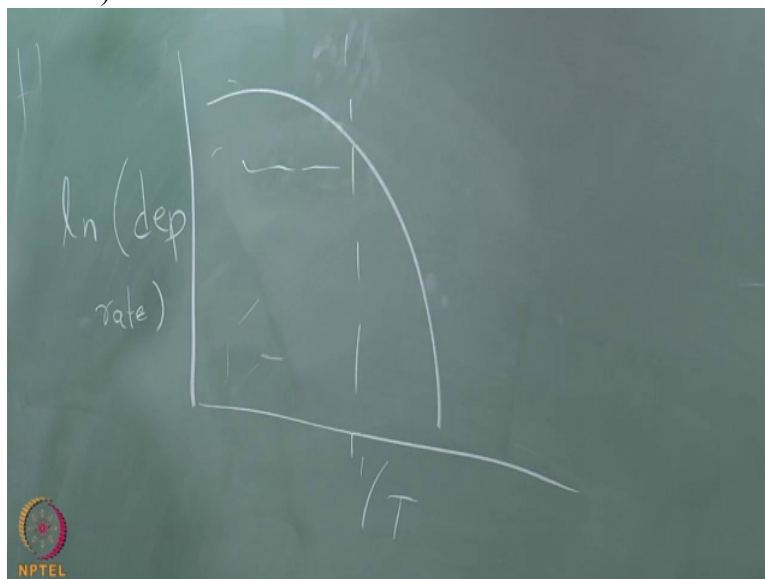


The correct answer is actually 4. This is how most CVD deposition rate curves look like.

Now what does that mean?

So there is essentially a region

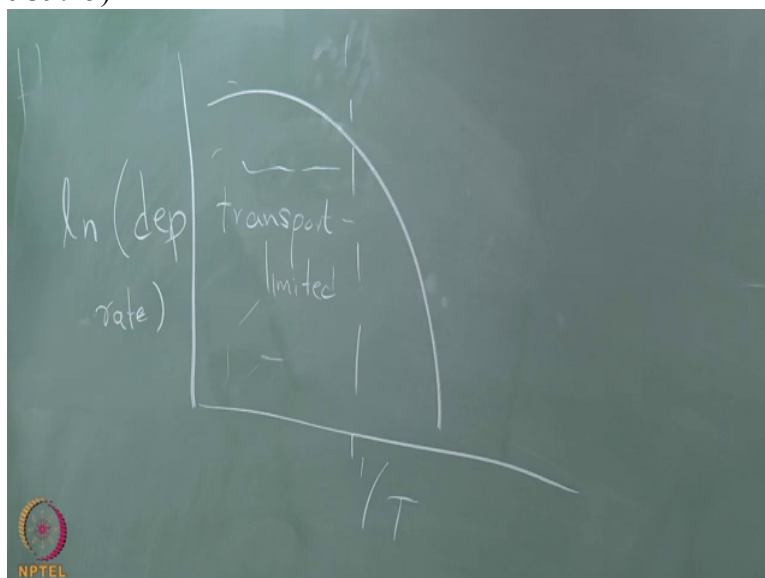
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where the deposition rate is virtually insensitive to temperature, right? So what does that mean? What is the limiting factor? It is insensitive to temperature and we have said before that, chemical reactions are much more sensitively affected by temperature compared to transport reactions, I mean transport phenomena.

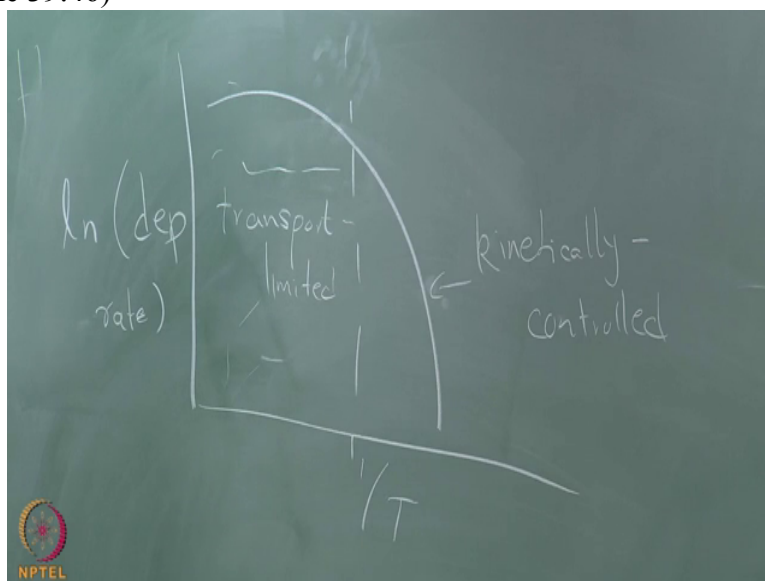
So what it means is that in this region where the deposition rate is virtually constant or slowly varying with respect to temperature we call that the transport limited region

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and of course by extension then, the region where you see very sensitive dependence of the rate of deposition to surface temperature, you would call this a kinetically controlled region.

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Another way to state it is this is the region of very high temperature, right?

So as you increase the substrate temperature, eventually it gets to be so high that there is no kinetic limitation. The reaction will proceed as long as reactants are delivered to the reacting surface. Whereas in this limit, the temperatures are low enough that even small variations in temperature can have very significant influences on the rate of deposition.

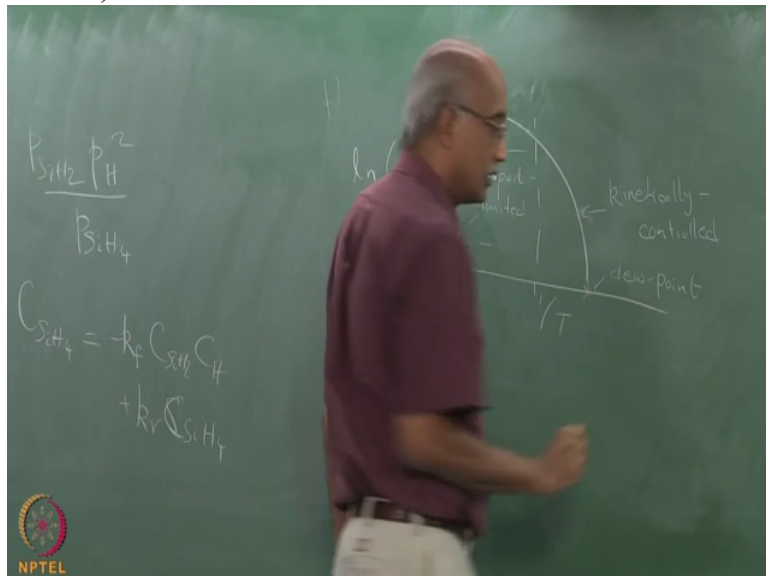
And by the way the point where this rate of deposition reaches zero is known as what? Any idea? Something we encounter all the time in daily life? What do you call the point at which either a pre-existing deposit does not deposit any more or the point at which the deposit first starts appearing on a surface?

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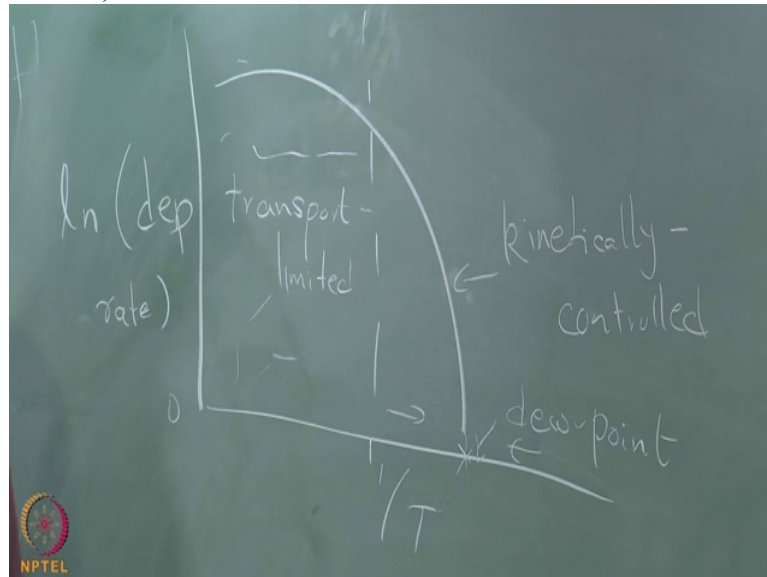
Dew point.

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Because you are all familiar with dew point in the case of water condensing and so on, but one thing that is unique about dew points in C V D systems is that they are not unique. In other words, depending on whether you approach the dew points in this direction or in this direction,

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the dew point may be different.

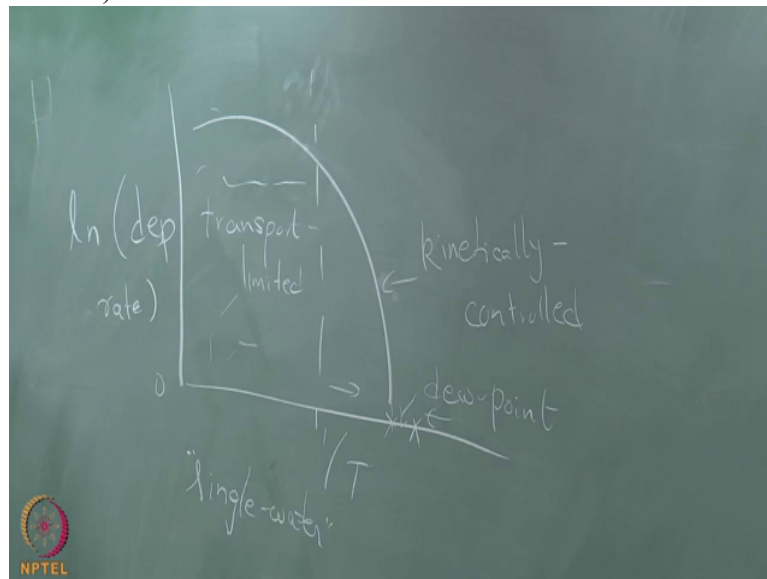
So we will talk about that in more detail because that is a very, very crucial thing to understand in C V D reactors. And in fact the behavior of the film between the two dew points, it is like a hysteresis effect, very simply. But when the temperature is between these two dew points, the film has some very, very interesting characteristics that can be exploited for certain applications.

So what does it mean? What it means is if you are in this high temperature region where you are transport constrained, the design of the reactor must pay a lot of attention to the flow dynamics because what this means you are transport-limited. That means you have to maximize and optimize your transport mechanisms.

So you have to ensure that the reactants are being fed in at the right rates, that all the flow patterns inside the reactor are being maintained absolutely stable. You cannot allow for even slight variations in the flow dynamics of the system. And it also means essentially that you can only process one wafer at a time because when you have a cassette of wafers, it is going to be very difficult to control flow dynamics around each one of them.

So typically this process is used for what is known as single wafer processing where you deposit

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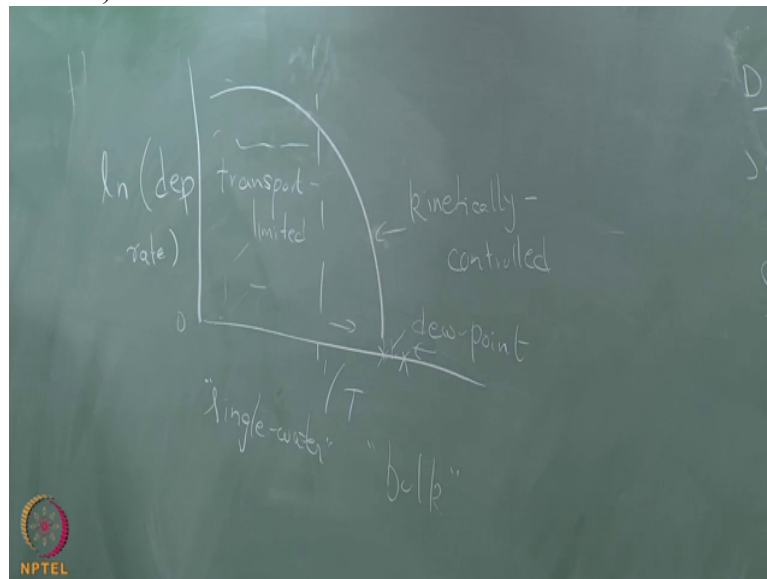


the film one wafer at a time. Again the primary reason for this is it is virtually impossible to control flow very tightly around the entire basket or cassette of carriers. On the other hand, in this region what this means is that your flow control do not have to be very tight except as far as they effect the temperature distribution.

But what we need to control very, very carefully here is your temperature distribution. You have to make sure that the temperature profiles are maintained absolutely constant. You have to have the best possible control mechanisms for temperature just as you want to have the best possible control mechanisms for flow in this condition, right. So from the process control strategy viewpoint, where you focus is very, very different in these two cases.

So a lot of very interesting things you can actually extract from this work, from this figure. One of the things again is this is essentially suitable for bulk C V D where you try to process many, many wafers at one time. So you are into volume production where we have to make a lot of product, then you are probably better of trying to operate in this region.

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Whereas if the throughput is not your primary requirement but rather the control and the purity and the uniformity of the film then you are better off working in this region.

So if you look at this figure and we will keep coming back to this, there are a lot of very interesting inferences you can draw regarding how CVD process functions in these two limits and what are the design considerations for CVD reactors operating in these two limits. But this is a universal figure. It does not matter which CVD process you look at, or which CVD reactor in what configuration, you will always come up with this.

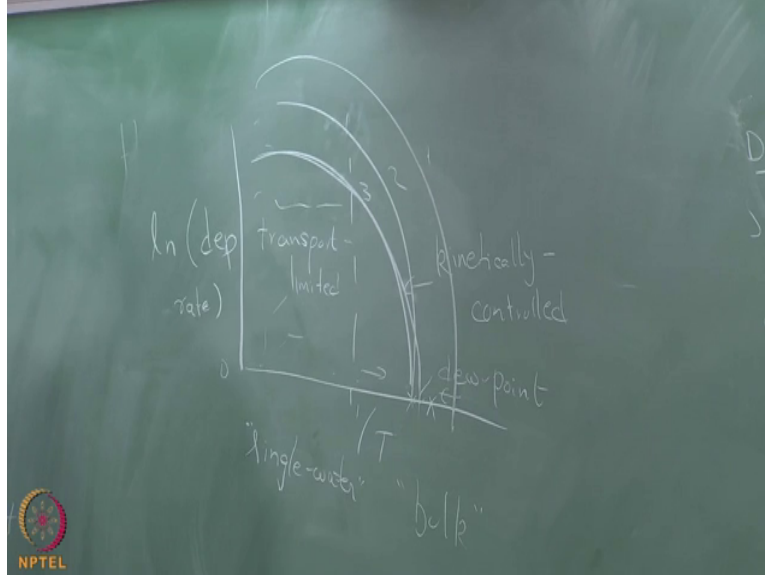
Although I should mention that there is one case where you will have a reverse behavior and that is in a very rare case where a CVD film is more favorable at lower temperature and becomes unstable at a higher temperature. Obviously in that case, everything will now kind of turn around. And in fact some of the naturally occurring CVD films that we will talk about later like you know the tungsten condensation of the bulb wall or even this hot corrosion due to molten alkalis, those are actually deposits that are more stable at lower temperatures compared to higher temperatures. So everything will now become the mirror image.

One of the things you may also want to think about is, in this system suppose you double the flow rate of the reactants or effectively double the concentration of the reactants. How is this figure going to change? How is this curve going to shift? So let us say that you know,



increase the reactant concentration by 2 x, will this whole thing shift like this? Or like this? Or it won't change? 1, 2, 3 what you choose?

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When you double the concentration of the reactants you do not change the dew point, right? So eventually it will converge like this. So, because the concentration only makes the difference in the transport limited region. Once you get to the thermodynamically constrained region, it has less of an influence. So eventually the figures will converge and you will essentially come to the same dew point.

Anyway as I said lot of interesting things to think about, so in the next class we will, this class we primarily dealt with the thermodynamic aspects. From the next class we will spend some time talking about transport aspects in a C V D reactor. Any questions? Ok, see you in the next class.