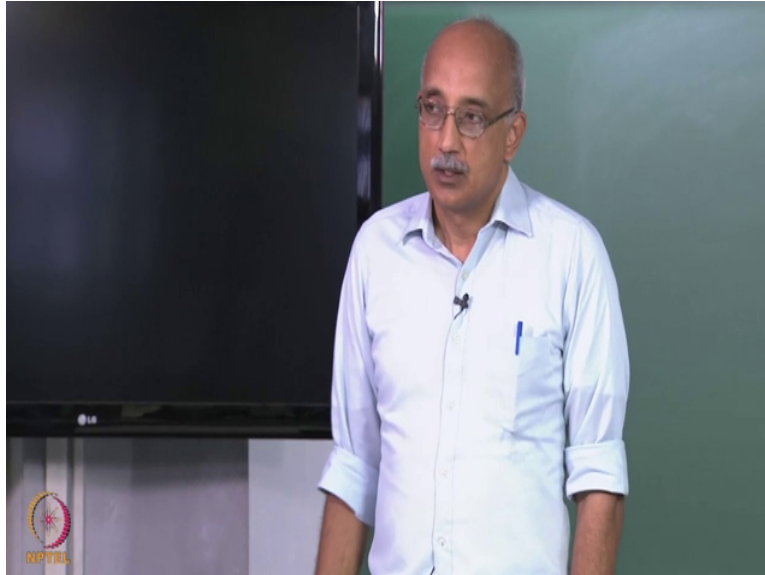


Chemical Engineering Principle of C V D Processes
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Lecture No 13
C V D in Tungsten Filament Lamps: Design Aspects

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Good morning and welcome to the next lecture in our class on Chemical Engineering principles of C V D process. In the last lecture, we started dealing with a specific illustration of C V D where we were looking at tungsten filament bulbs and the process involved in the blackening of the bulb due to the deposition of tungsten from the filament.

Again the, the history of tungsten filament bulbs changed from P V D to C V D. Because initially we were just burning carbon filaments which had a very high evaporation rate so the bulbs would become black within days and you could not use them any more. Then we started using tungsten filaments which burnt with a lower evaporation rate. So it extended the lifetime but still you were looking at weeks of lifetime.

So the next advancement was actually filling the bulb with an inert gas which slowed down the rate at which the deposition happened and extended the lifetime again to months instead of weeks; but still a very finite lifetime. And all involving essentially physical vapor deposition because tungsten was eva/evaporating, carbon or tungsten was evaporating from the filament and depositing as carbon or tungsten on the bulb wall.

So the major advancement in the lighting industry which was actually pioneered by General Electric was to fill the bulb with halogen gases. When you do that, you produce a reactive environment and you set up a C V D process in which the tungsten that is deposited on to the bulb wall reacts with the halogen that is inside the bulb to produce the halide molecule in the vapor phase which cycles back to the filament.

So essentially you set up something called the halogen cycle where you are constantly forming a tungsten halide at the bulb wall which is decomposing into tungsten at the filament. So if we set up the cycle properly, conceptually it is possible to design a bulb with infinite lifetime. The rate at which the tungsten is evaporating from the filament can be exactly balanced by the rate at which it is getting re-deposited on to the filament.

And the point I made in the last class is the industry has actually reached this state of almost perfect design, in that bulbs today do not fail for simply blackening. What they fail for is the filament actually snapping. Of course when that happens, you get a huge spurt of tungsten which deposits on the bulb and makes it very, very black.

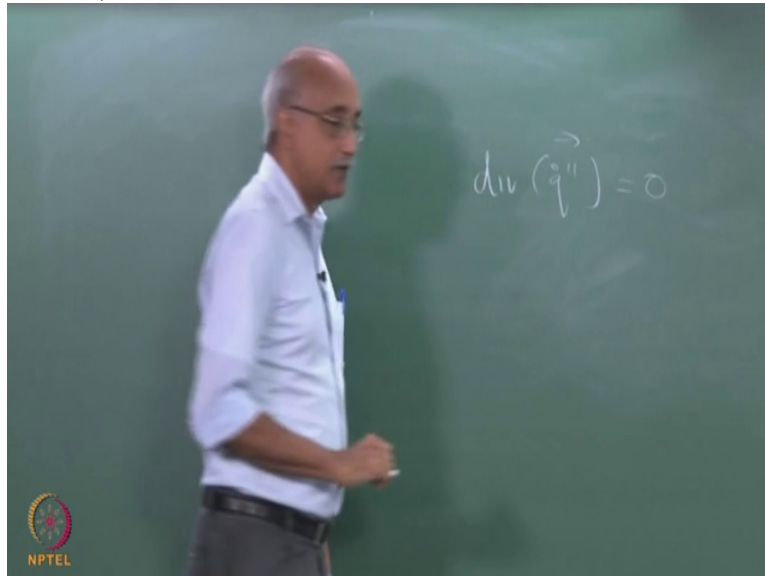
But the sustained and continuous evaporation and deposition of tungsten on the walls of the bulb has pretty much been eliminated in the lighting industry now. So it is a great advancement from a technology viewpoint where, it is a very interesting application of C V D technology because you are relying upon vapor phase reactions to convert the depositing element into various species in the gas phase which have different migratory paths.

The tungsten species in the gas phase goes from the filament to the bulb but the tungsten halide species in the gas phase goes from the bulb to the filament and it is the balance between these two that gives you the no-blackening condition.

We then started doing the transport analysis of the system and the simplest way to modulate is where we model the entire enclosure of the bulb as a stagnant layer. And this is called the Langmuir layer which can extend all the way from the filament to the wall of the bulb and by definition in a Langmuir layer the transport only occurs by diffusion or conduction. There is no convection process involved.

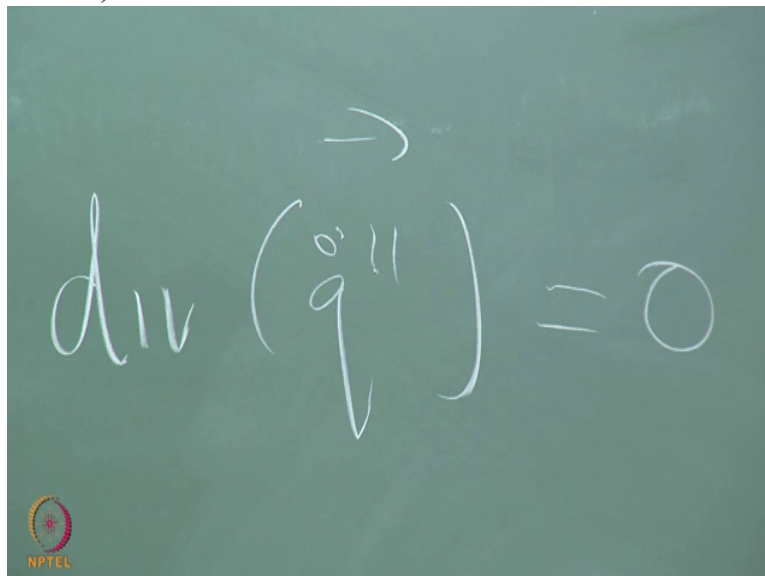
So under that simplifying assumption you can write the heat transfer equation as divergence of \vec{q}'' equals zero

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where again \vec{q}'' stands for heat transfer per unit area per unit time. The dot stands for per unit time. The double prime stands for per unit area.

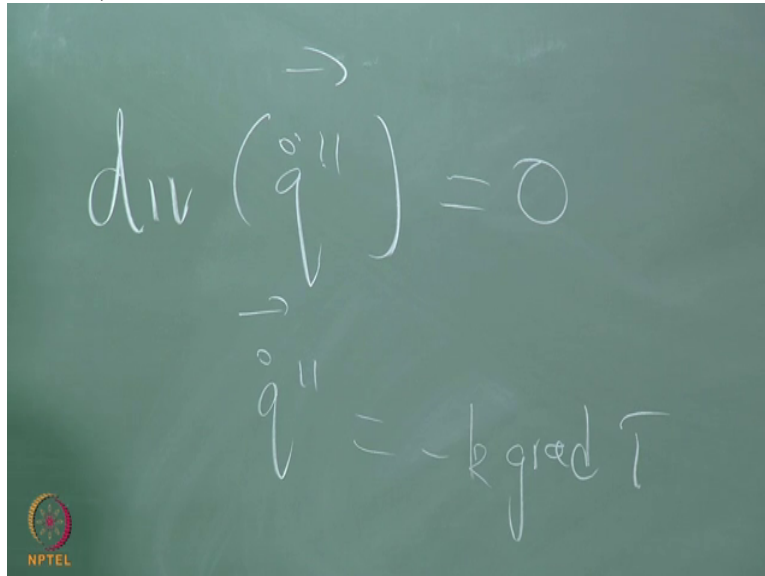
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So it essentially represents a flux.

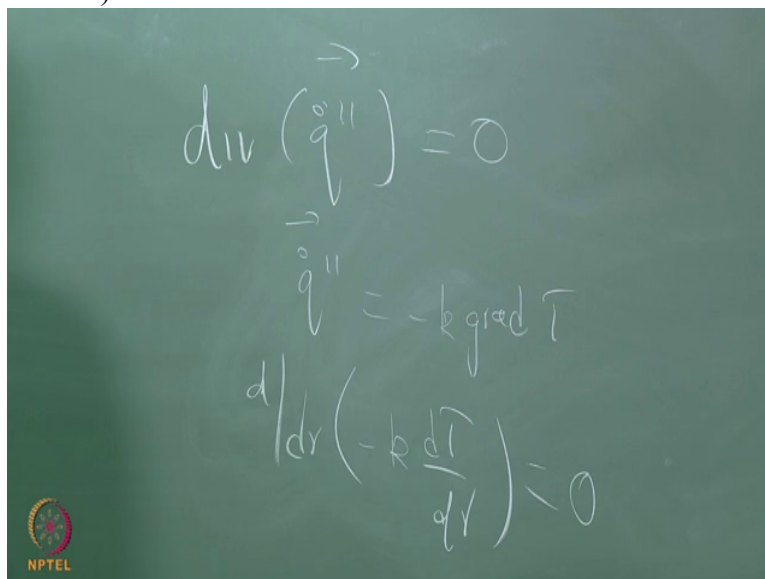
Basically saying that in a stagnant Langmuir layer, the heat, the divergence of the heat transport flux equals zero. Of course if you are talking about a simple, of course \vec{q}'' can be written as minus k gradient in temperature. And

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$$\text{div}(\vec{q}'') = 0$$
$$\vec{q}'' = -k \text{grad} T$$

in the simple radial, transport situation you can write this as $\frac{d}{dr}$ of $-k \frac{dT}{dr}$ equal to zero and solve for the

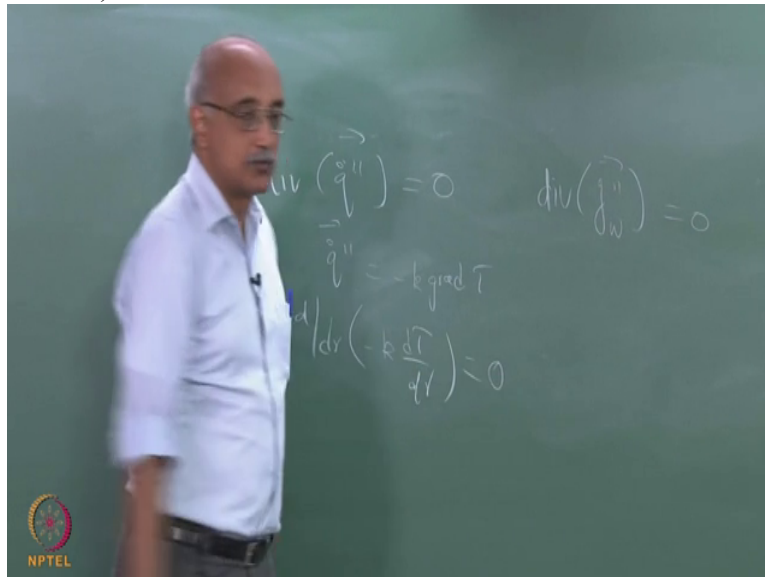
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$$\text{div}(\vec{q}'') = 0$$
$$\vec{q}'' = -k \text{grad} T$$
$$\frac{d}{dr} \left(-k \frac{dT}{dr} \right) = 0$$

temperature distribution inside the bulb.

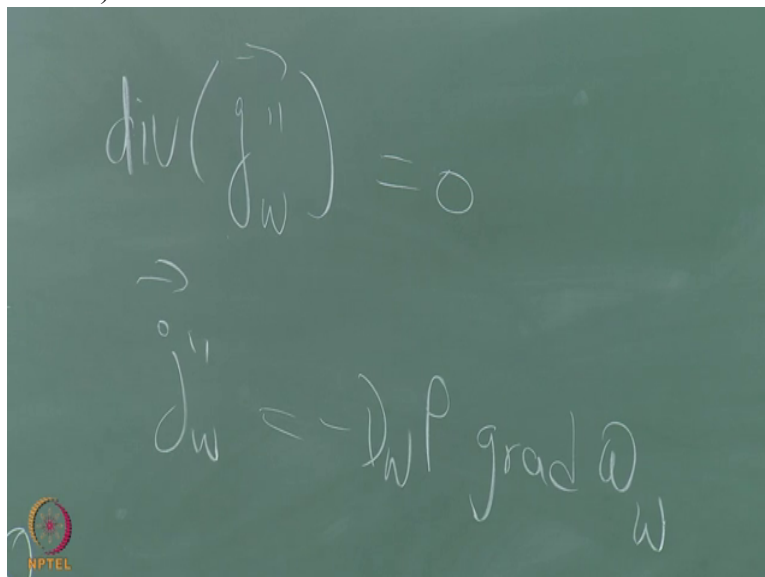
And similarly you can write an equation for the diffusive flux of tungsten from the filament to the bulb and that will, you will then write it as divergence as $\text{div} j'' = 0$ where this is the diffusive flux of

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tungsten towards the wall of the bulb and j_w'' can then be written as minus $D_w \rho \text{grad } \omega_w$ which is the Fick diffusion form of the

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flux equation for mass plus there is a thermal contribution to this, so you write that as plus $\omega_w \alpha_w T \times \ln T$ over T , sorry it should be $d T$ by T or $d \ln T$ and this is, represents the thermal diffusion portion because

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$$\text{div}(\vec{j}_w) = 0$$
$$\vec{j}_w = -D_w P \left[\text{grad } @_w + w_w @_w T + \frac{dT}{T} \right]$$

mass transfer can happen not only by mass diffusion but also by thermal diffusion. When there is a temperature gradient that can also drive mass transfer.

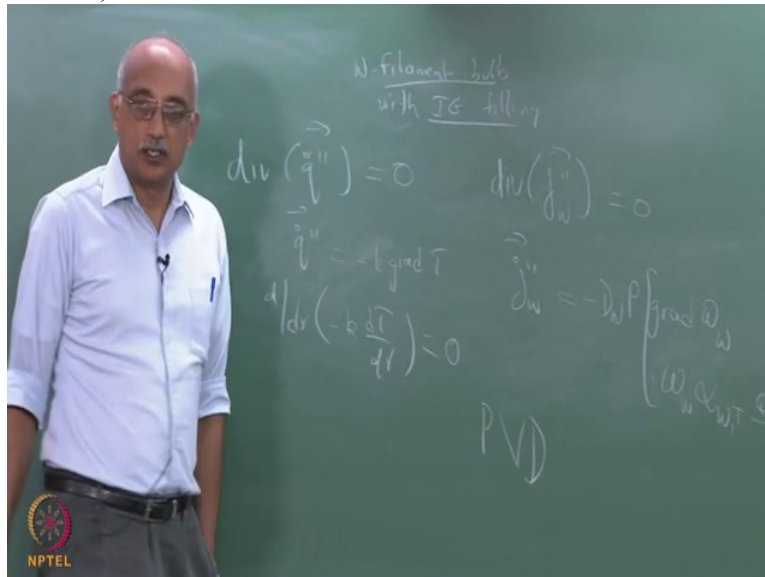
So the, and again, this is for the simple case of a tungsten filament bulb with inert gas filling. So there are no

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W-filament bulb
with IG filling

chemical reactions. This is essentially a P V D process and it says there is a temperature distribution that is set up inside the bulb. And there is an

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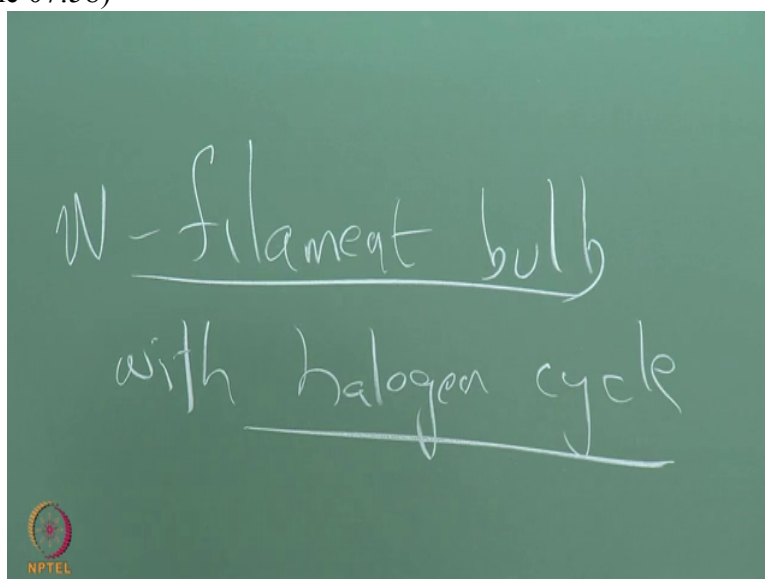


associated diffusive flux of tungsten and it is all one way. There is nothing to bring the tungsten back to the filament.

So there is a finite rate of mass loss from the filament which keeps happens till the filament becomes too thin at which stage it snaps. Or so much tungsten deposits on the bulb wall, the light does not come out. Right? Those are the failure modes in this lamp. Now the halogen cycle lamp is where you have a tungsten filament bulb with halogen cycle.

So in this case

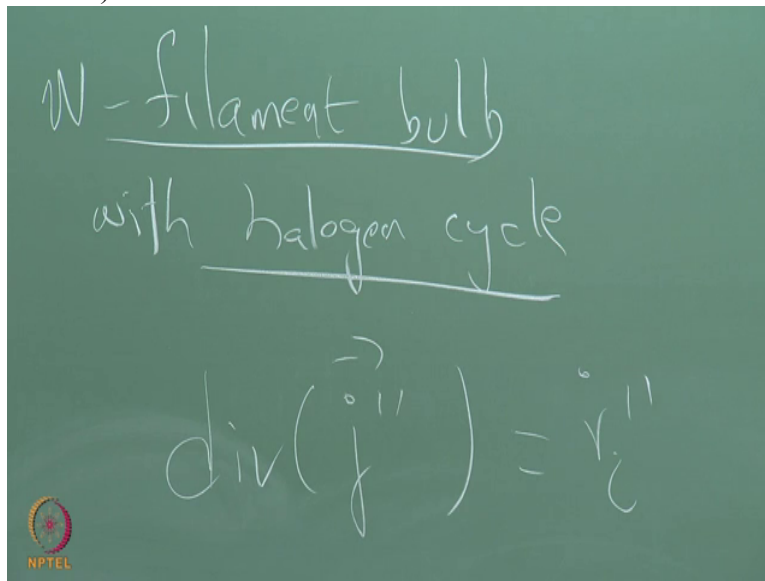
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you have set up chemical reactions. As soon as you introduce a reactive species into the bulb, you start forming various chemical compounds due to chemical reactions. It is not inert anymore which means that your mass transfer equation cannot be written as $\nabla \cdot \mathbf{j}_i = 0$, divergence of \mathbf{j}_i equal to zero.

Instead you have to write it as $\nabla \cdot \mathbf{j}_i = r_i$ where the diffusional flux of species i ,

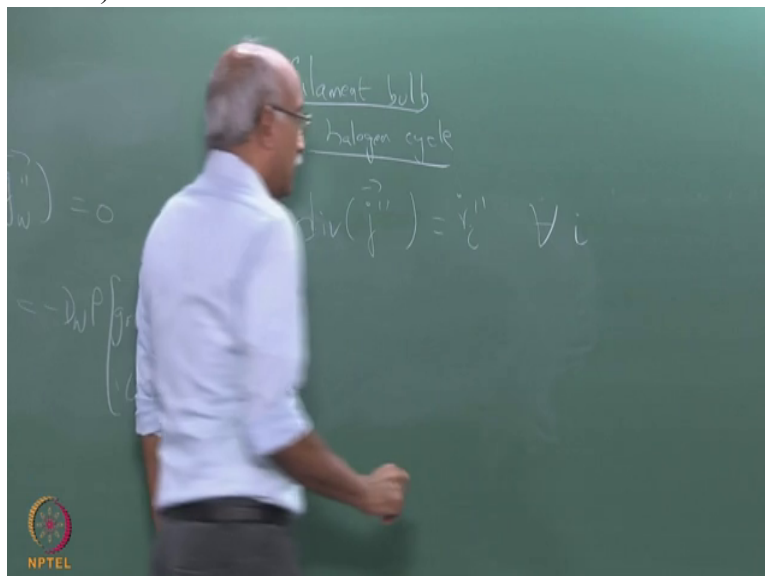
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the divergence of that must now be balanced by the rate at which that species i is reacting.

So you have to write it for all i ,

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which are all the chemical species that are present in the system and you have to write this j_i , so this is for any i, j j_i dot double prime and that is equal to minus rho d i gradient in species i plus omega i alpha i t times d T by T.

So this is the

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N-filament bulb
with halogen cycle

$$\text{div}(\vec{j}_i'') = r_i'' \quad \forall i$$

$$\vec{j}_i'' = -\rho D_i \left[\text{grad} \omega_i + \omega_i \alpha_{i,T} \frac{dT}{T} \right]$$

generalized form of the species diffusion equation in the case of reactive environment. Now the problem is, while this can be solved analytically and there are actually literature solutions available for this particular case, that case is a lot more complex because we do not know this.

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N-filament bulb
with halogen cycle

$$\text{div}(\vec{j}_i'') = r_i'' \quad \forall i$$

$$\vec{j}_i'' = -\rho D_i \left[\text{grad} \omega_i + \omega_i \alpha_{i,T} \frac{dT}{T} \right]$$

As I have said before when you have a highly reactive environment and you have multiple elements present, the number of chemical species that can form are literally in the hundreds. And the number of chemical reactions that can happen are also in the hundreds. So how do you specify this r_i double prime?

For every species you have to know every chemical reaction it is involved in. You have to know every chemical reaction that produces that species and every chemical reaction that consumes that species and you have to obtain a net reaction rate. It is not doable.

I mean you can approximate it and in fact what people have done in the past is to try and represent the dominant chemical reactions by a series of maybe 10 reactions or so and assume that, that completely describes the chemically reactive environment inside the bulb. But that is a necessarily restrictive and you could make significant errors by taking that approach.

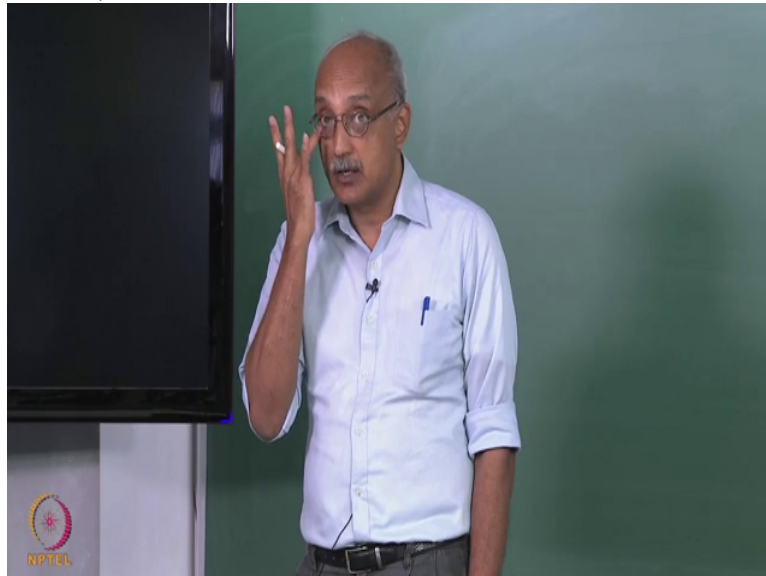
So the latest iteration of this is to come up with a smarter way of doing this modeling, right? So supposing we want to use this methodology for a chemically reactive environment, how would you do that? Is there a shortcut that you can think of which will enable us to do that? What is that in a chemically reactive environment that behaves like a chemical species in a non-reactive environment?

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The chemical element. Because the element even in a

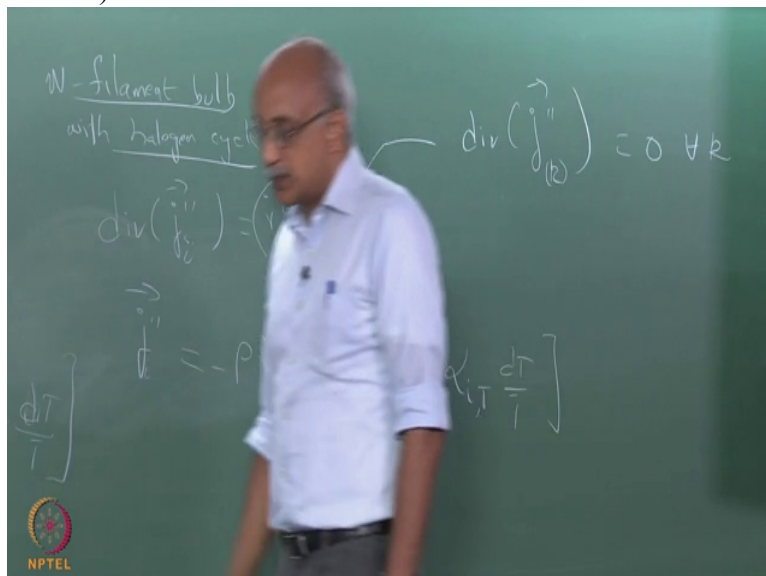
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reactive environment cannot be generated or consumed unless it is a radioactive element and I hope that we do not have any radioactive species in our bulbs. So if you rewrite these equations in terms of elements, in this case you can go back to that form.

So for the same case of the tungsten filament bulb with halogens inside the bulb, you can now write this as divergence of \vec{j}_k double prime equal to zero for all k where k

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represents the elements that are present in the system. So for example in the case of the tungsten filament bulb, if your halogen that you have introduced inside is, let us say hydrogen bromide and your filament is tungsten, then there are only 3 elements in the system, tungsten, hydrogen and bromine.

The number of chemical species can be many, many depending on the various reactions that take place but the number of elements is only 3 and these elements are conserved. They are not; there is no reaction term, there no net reaction term. And similarly you can substitute this expression with $j_k \cdot \text{double prime} = -\rho D_k \text{ times gradient in } \omega_k \text{ plus } \omega_k \alpha_k$ where now this is the corresponding diffusional flux of the

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The image shows a chalkboard with two equations written in white chalk. The top equation is:

$$\vec{J}_k = -\rho D_i \left[\text{grad } \omega_i + \omega_i \alpha_{i,T} \frac{dT}{T} \right]$$

The bottom equation is:

$$\vec{J}_k = -\rho D_k \left[\text{grad } \omega_k + \omega_k \alpha_{k,T} \frac{dT}{T} \right]$$

In the bottom equation, the terms D_i , ω_i , and $\alpha_{i,T}$ are circled in red. An NPTEL logo is visible in the bottom left corner of the chalkboard image.

kth element, D_k is the diffusivity of the kth element.

Now that is not a real quantity, right? Because elements do not diffuse. Elements are contained in species that are diffusing. But because of that you can obtain a net effective diffusivity of the element which is a weighted sum of the diffusivities of the species containing that element. And similarly for $\alpha_{k,T}$, the thermophoretic diffusivity of the kth element is actually a fictitious number but it represents the effective thermal diffusivity of the kth element.

And for example you can write D_k , the effective diffusivity of the kth element as being equal to summation over i of $\omega_{k,i} \text{ times } D_i \text{ times gradient in } \omega_i$ divided by summation over i of $\omega_{k,i} \text{ gradient in } \omega_i$ where $\omega_{k,i}$ is the mass fraction

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$$D_k = \frac{\sum_i \omega_{(k),i} D_i \text{grad } \omega_i}{\sum_i \omega_{(k),i} \text{grad } \omega_i}$$

of the kth element in the ith species. D_i is the Fick diffusivity of the ith species and gradient in ω_i is the gradient in the mass fraction of the ith species.

So you take the sum and divide it by the sum of $\omega_{(k),i}$ times gradient of ω_i that will yield an effective diffusivity, Fick diffusivity of the kth element. So back into this term, so we know how to define D_k , we know how to define $\omega_{(k)}$, $\omega_{(k)}$ times...by the way $\omega_{(k)}$ will be summation over i of $\omega_{(k),i}$. It is the total

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$$\omega_{(k)} = \sum_i \omega_{(k),i}$$

mass fraction of the kth element in the system and then $\alpha_{k,t}$, the thermophoretic diffusivity of element k can similarly be obtained by summation over i of $\omega_{(k),i} \alpha_{T,i}$ divided by summation over i of $\omega_{(k),i}$.

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The image shows a chalkboard with a handwritten equation for the effective diffusion coefficient $D_{(k),T}$. The equation is written as a fraction where the numerator is the sum of the product of the weight fraction of the kth element in species i, $W_{(k),i}$, and the weight fraction of species i, W_i , multiplied by the diffusion coefficient of species i, $D_{T,i}$. The denominator is the sum of the product of $W_{(k),i}$ and W_i . An NPTEL logo is visible in the bottom left corner of the chalkboard image.

So you can estimate the effective Fick diffusivity and thermal diffusivity of the kth element and substitute those into those equations and you can now obtain the diffusion flux of the kth element. Now that is very important because in a CVD environment of a halogen cycle lamp what you really care about is, is that going to be tungsten deposition happening or not?

So what you want to estimate is this quantity j_W which is the effective

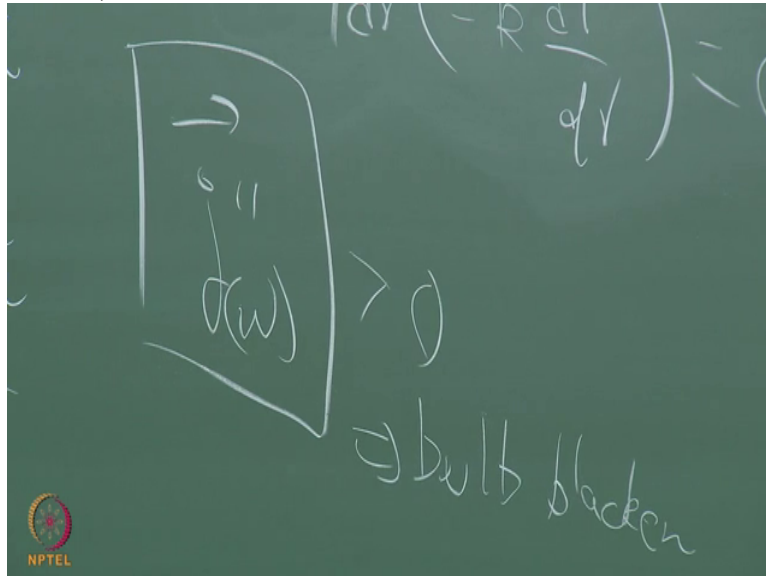
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diffusional flux of tungsten element, not tungsten species. Again you have to be clear in your mind about the difference between the two. In a tungsten lamp, tungsten species is only one species which is tungsten in the gas phase. Tungsten element can be contained in a hundred species that contain tungsten as an element.

So what we are talking about here is the diffusivity of tungsten as an element which occurs because of diffusion of various species containing that element tungsten. If this diffusivity is greater than zero, this implies that the bulb will blacken. That is, if there is a net deposition flux of

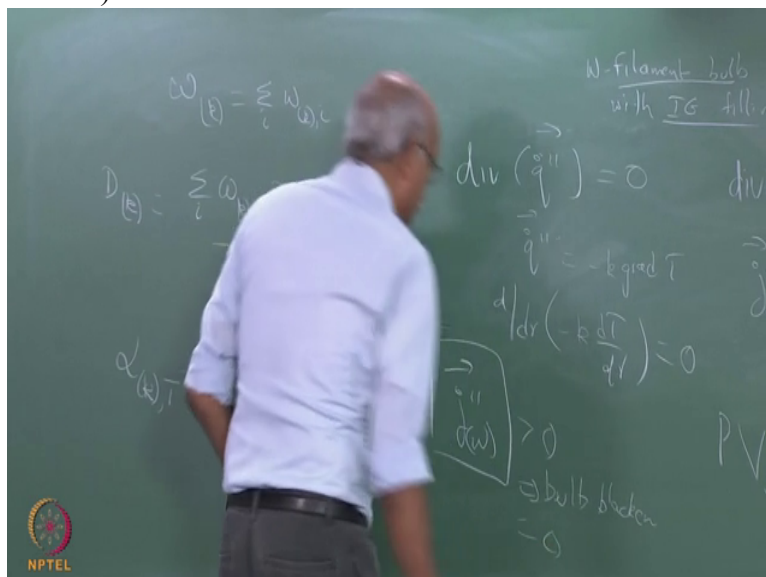
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tungsten element towards the wall of the bulb then it will form a film on the surface and the bulb will start blackening.

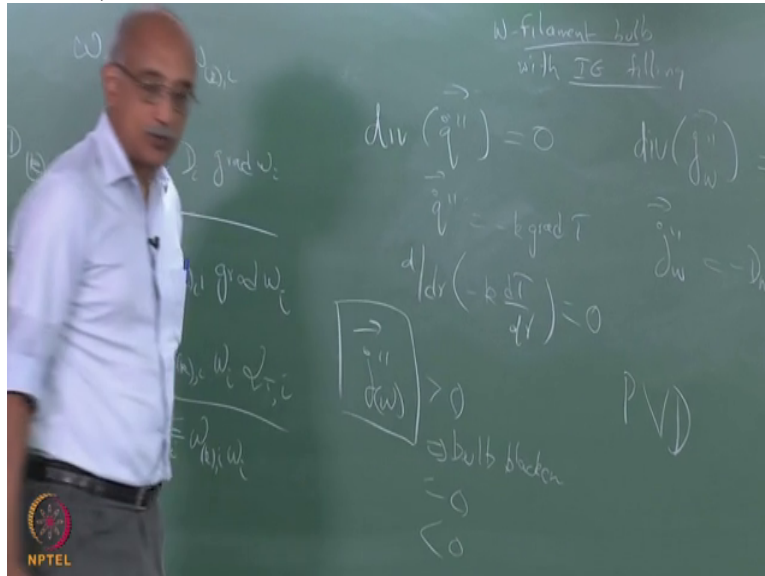
If this is equal to zero

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then there is no bulb blackening. So the bulb will remain clear. If this is less than zero,

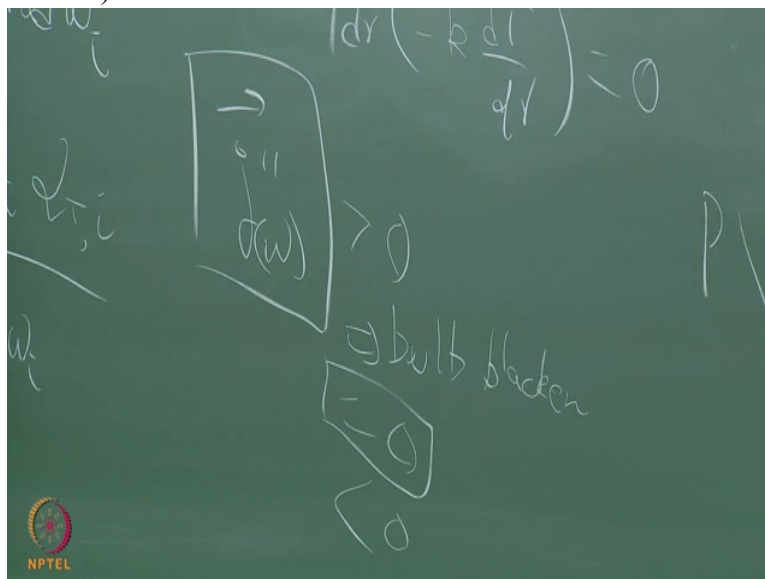
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the transport will actually be reversed and tungsten will now start accumulating on the filament. Now that is a little unlikely to happen because the, the equilibrium is set up so that the transfer, I mean the bulk of the tungsten is in the filament, right?

So it is much more likely that the flux will happen from the filament towards the bulb rather than the other way round. But theoretically it is possible for the diffusive flux of tungsten element to be negative towards the filament. But what the ideal situation that we want to look for is this. We want to set up the conditions of

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the bulb in such a way that for a very long period of time, the net flux of tungsten towards the wall is zero or negative.

So how do you do that? The fill gas, let us say you are using hydrogen bromide, or you are using oxy bromine, you control the concentration of the fill gas so that the resulting distribution of species inside the bulb results in a net flux of zero for tungsten element to the wall. So the, the fill conditions. the nature of the gas, the chemical composition of the gas, the molecular weight of the gas all play a role in determining the fluxes, mass fluxes that result in the bulb.

Another parameter that you can have control over is the filament temperature. You want to run the filament temperature high in order to get maximum illumination but at the same time as you increase the filament temperature, the rate of evaporation increases. So the net amount of tungsten that is present in the bulb environment increases.

So in that sense you want to arrive at an optimal filament temperature which maximizes the luminosity that it provides while minimizing the tungsten loss due to evaporation. The other parameter that you have some control over is the pressure inside the bulb. You know what is the pressure at which you fill the gases and you seal the bulb.

Now typically in the old days, there used to be vacuum. But obviously that is the worst case. Because when you have a vacuum environment. Diffusion is greatly accelerated and the filament will burn out very quickly. So the more pressure you have inside the bulb, the slower will be the rate at which the tungsten molecules will leave the filament and try to go to the walls of the bulb but here again there is a trade-off.

You know, you do not want to pressurize it so much that you know, the bulb will burst. Or the cost is very high. So there is an optimal pressure to be maintained inside the reactor so that you get the best characteristics of both filament life as well as process economics.

Of course the other critical parameter over which you probably do not have much control is the bulb temperature itself. Because that is going to be set by, once you set the filament temperature and once you know what the outside temperature is, the bulb temperature will be some equilibrium between these two temperatures. So you really do not have much, by way of control over that.

The other parameter over you do have some control over is the material of which the bulb is made. For example, you know most of these bulbs are glass, right and glass has a certain surface energy. If you can, for example, make the bulbs of a lower surface energy material, that can actually reduce the rate at which tungsten molecules deposit, it will essentially repel them. In the, in the extreme case you can think about a bulb which has a coating inside which is an anti-deposition coating which will actively repel these molecules and push them away.

So there are some parameters that you can try and control in order to maximize the rate, maximize the lifetime of, of the bulb. But the analysis essentially has been greatly simplified by restating the equations in terms of element properties rather than species properties. And that is something you should remember when you are analyzing any C V D reaction system.

If you try to do your analysis in terms of the chemical species, the, the analysis will quickly become very complicated and there will be a lot of uncertainties and unknowns introduced because of the assumptions that you necessarily have to make about the various reactions that are taking place.

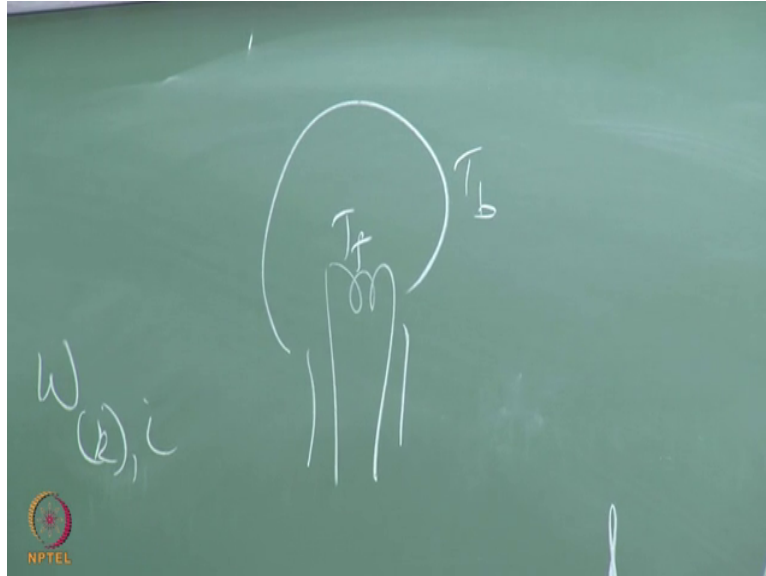
On the other hand if you restate it in terms of the chemical elements that are present, the fact that elements cannot be destroyed or created means that you can essentially simplify the analysis quite significantly and obtain analytical solutions in most cases.

Now in terms of, you know the operation of the bulb, the other major assumption that you have to make is whether or not you assume that chemical equilibrium prevails everywhere. We discussed this briefly in the last lecture. The filament temperature is very high. So it is very likely that you will be approaching chemical equilibrium at the filament and in the vicinity of the filament.

On the other hand, the walls of the bulb are essentially at room temperature. So it is very unlikely that you will have equilibrium prevailing at the bulb walls. So somewhere in between the nature of the problem changes from one which approaches thermo chemical equilibrium to one that deviates significantly from it.

So in terms of the essential analysis of this problem what we have assumed here implicitly is that you have what is known as a chemically frozen layer. The assumption that is typically made in this type of a problem is if you have a bulb with a filament which is at temperature T_f and the bulb is at temperature T_b and by the way

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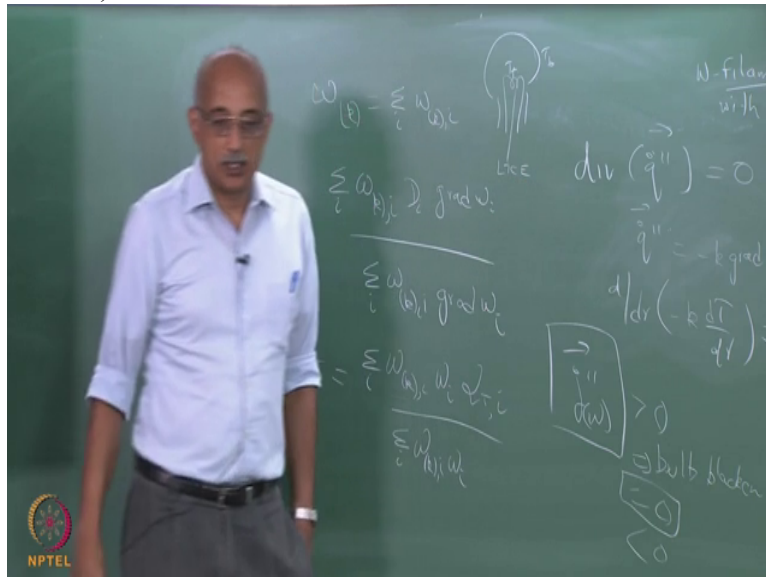


as I was mentioning in the last class the electric bulb can actually be redesigned as a C V D reactor.

This can be the source of your C V D material. And this can be your substrate on which the material deposits. So think of an electric bulb as a C V D reactor. It is the simplest form. It is actually given a name. It is called a filament C V D reactor. And the way that it works is exactly the way the bulb works.

Material is burning off the filament in the middle that is at the high temperature and then it is depositing on the substrate that is around it. So when you look at this situation T_f and T_b , here because of the very high temperatures you can assume that

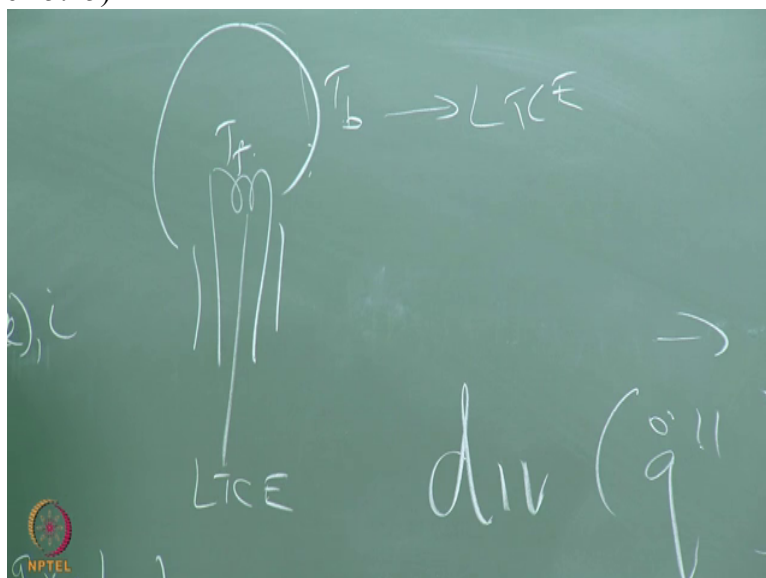
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local thermo chemical equilibrium prevails. At the bulb walls even though the temperatures are low, it is a heterogeneous situation.

You have a solid surface that is coming in contact with the vapor species. In a heterogeneous case, equilibrium is achieved much more easily compared to a homogenous case. So for the simplicity of analysis, typically we would assume that chemical equilibrium also prevails at the walls

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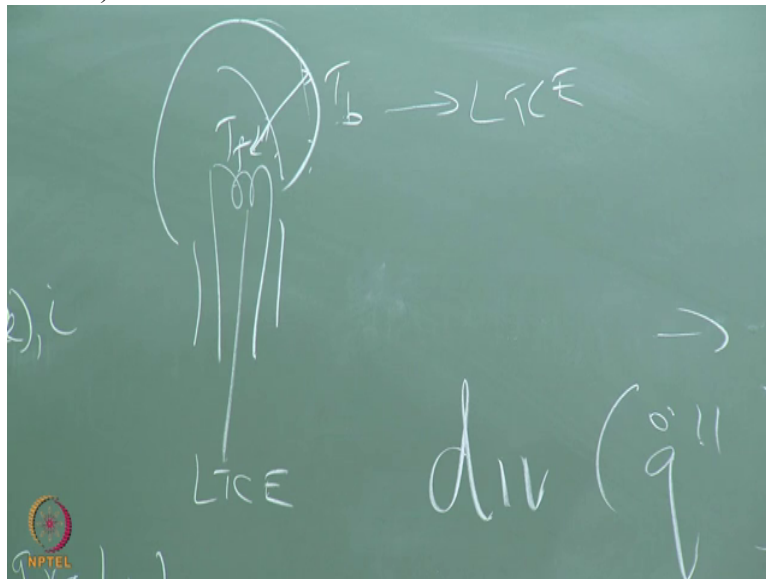


of the bulb.

So in between, between the filament and the bulb, you have some flexibility in terms of what assumptions you make. You can assume that thermo chemical equilibrium will prevail, let us say, up to half the distance from the filament after which kinetics will take over.

Or you can assume that thermo chemical equilibrium extends all the way to the bulb walls. You assume

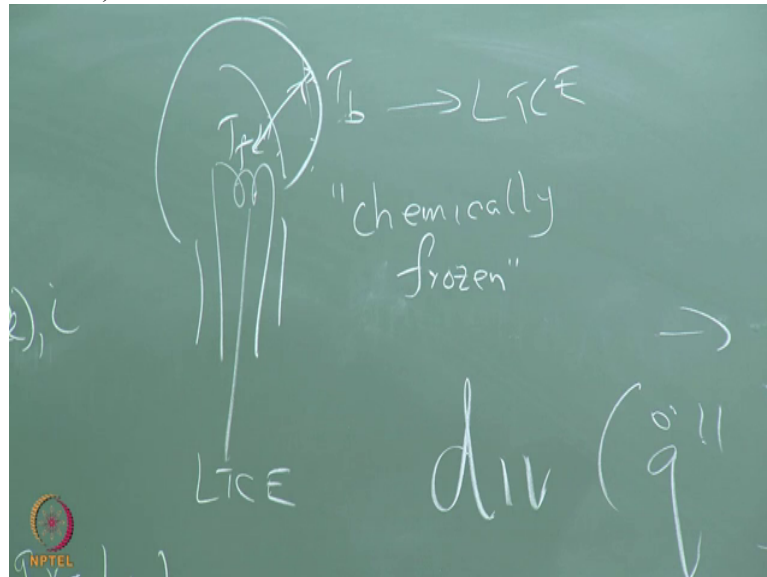
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that it is a sufficiently high temperature that it is justifiable to assume thermo chemical equilibrium everywhere inside the bulb. That is another approach.

The third approach is to say that you have thermo chemical equilibrium here and at the bulb wall. In between chemical reactions do not take place. And that assumption is termed chemically frozen. When you say

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that the region is chemically frozen, what it means is that chemical reactions are not allowed to take place.

And the species transport is completely controlled only by the diffusive phenomena that are present and there are no chemical reactions happening inside. Now obviously this assumption is not valid inside a bulb. You know it is very hard to justify it. In fact the place where this is justified is in a, in a, the next case that we will deal with, which is a boundary layer on top of a substrate.

In that case the boundary layer is thin enough that you can, for the sake of simplifying the problem ignore the chemical reactions that are taking place inside this boundary layer and only consider chemical reactions taking place on the substrate and at the outer edge of the boundary layer.

But in the case of the reactive environment like a filament CVD reactor or an electric bulb the more common assumption is to assume that the local thermo chemical equilibrium extends all the way to the bulb wall. The temperature distribution everywhere is such that you never deviate very far from thermo chemical equilibrium which enables us then to use free energy minimization as the method.

Once you know temperature distribution you use, you know an algorithm that minimizes free energy to calculate the corresponding species compositions at every temperature. And you

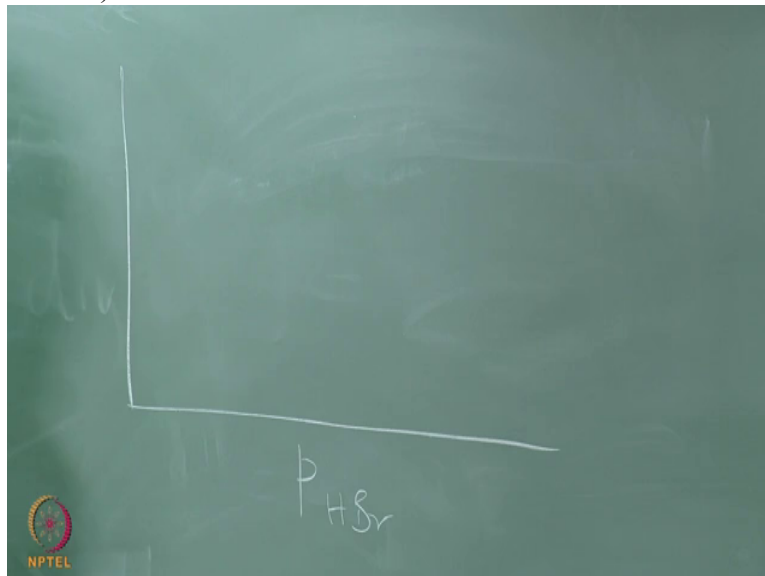
use the species compositions to calculate the gradients and once you know the temperature gradients and once you know the concentration gradients you can then proceed to calculate the diffusive flux of the species.

It is an iterative process in the sense that they have to be self-consistent. The temperature distribution that you obtain must be consistent with the elemental distribution that you obtain in the, in the bulb. So essentially you have to set up a loop where the two equations, the energy equation and the mass conservation equation are solved simultaneously in order to obtain a self-consistent solution.

Now in terms of the lighting industry how is this used? Well, one way is that you set the design windows basically. You decide on what is going to be your temperature; you know filament temperature, what is going to be your pressure and what is going to be your fill gas concentrations based on these types of analysis.

And in fact the way you would do this is to draw essentially dew point diagrams. So for example on the x axis you can draw the P of let us say H B r, the partial pressure

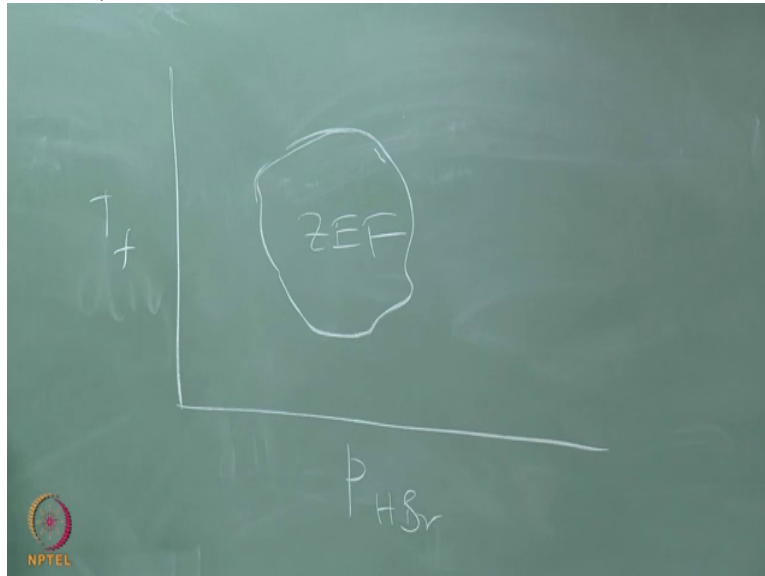
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of hydrogen bromide which is one of your fill gases and on the vertical axis, you can draw, let us say you use T f, the filament temperature as the parameter.

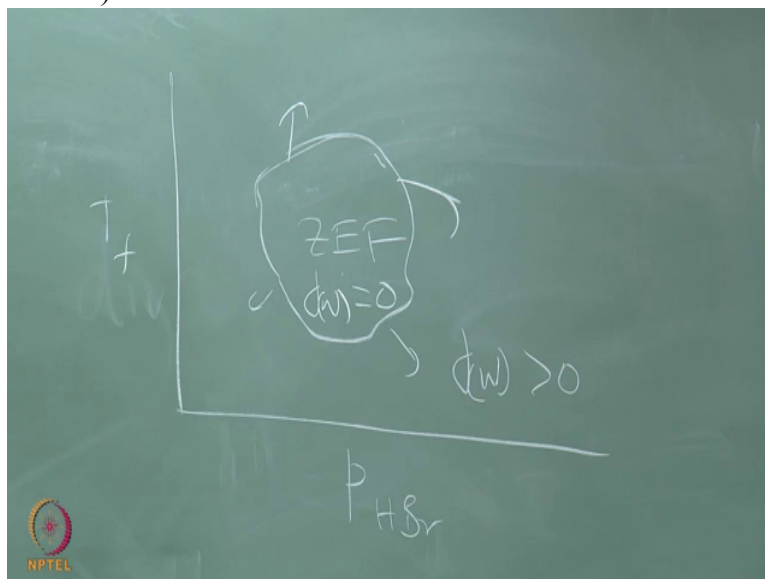
You will then map out a window which we call the zero element flux window,

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the Z E F window. If you are, if this combination of variables is in here, then you know that $j W$ is equal to zero whereas if you are outside this window then $j W$ is greater than zero.

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So you try to identify these operational windows and you select conditions for your bulb such that you are always inside this window of zero element flux. Of course the, you know this is very deterministic view but there are uncertainties. When we talk about this window the boundaries have certain error associated with them but hopefully if you have a good thermo chemical

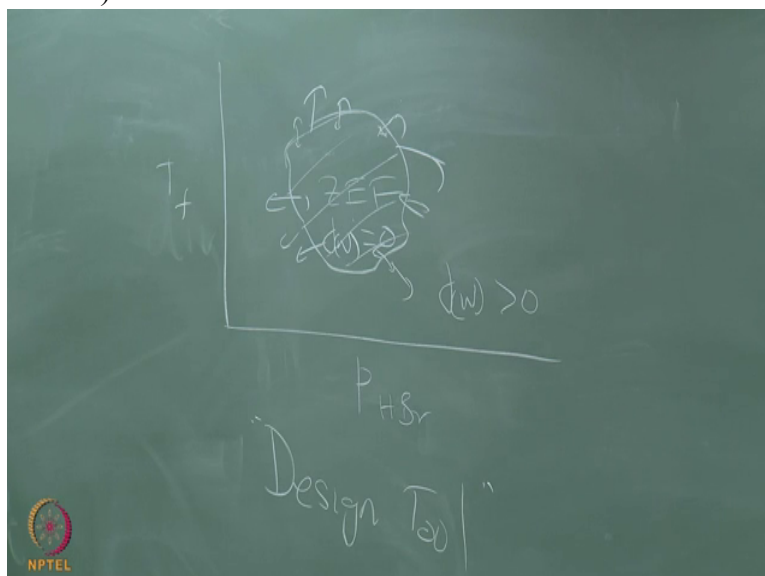
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database that contains the properties of all the species that are involved this uncertainty in the boundaries of this window can be kept to something as low as let us say, 10 percent. Ok.

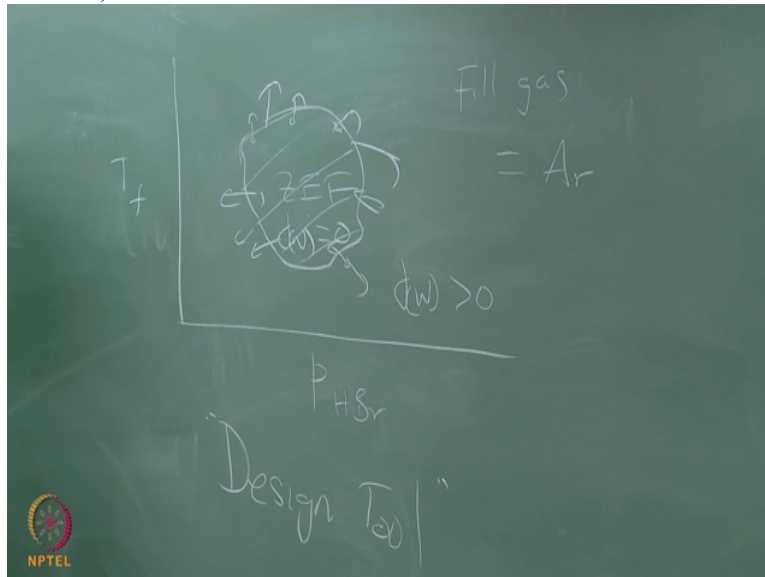
Then this becomes a very useful design tool for designing a bulb which has an extended lifetime.

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Another thing you have to be aware of are the parametric sensitivities. For example, let us say that in this particular case your, your carrier gas or fill gas may be argon, right. Because the HBr or halogen is only introduced in trace amounts.

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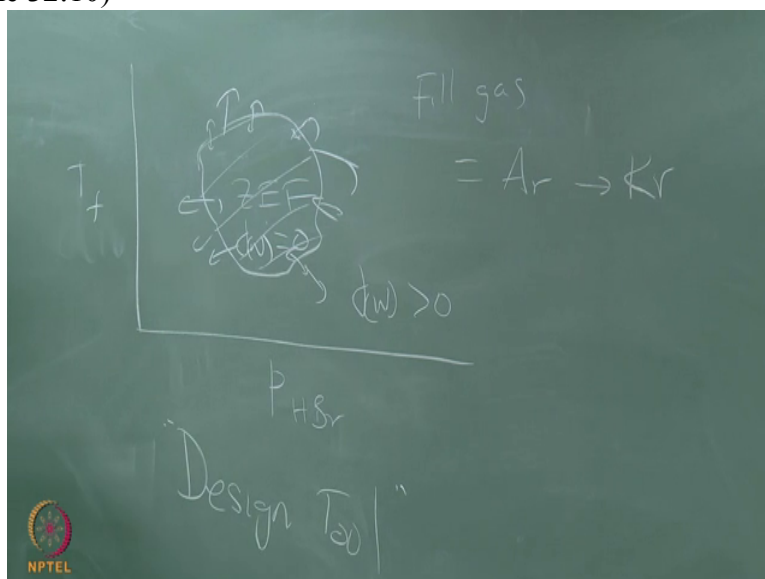


It cannot be used at the fill gas because it will be just too reactive.

So typically you use something like an inert gas as the primary gas to reduce, to slow down the evaporation process and then you use something like H B r or H O B r as your trace gas to produce the reactivity that you need but supposing now you changed from argon to let us say, krypton.

What would happen? Will that shrink the window?

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Will it expand the window? Or it will make no difference? Any speculation on that? Suppose you have a tungsten filament bulb and let us say you are using argon as the fill gas and then you change to krypton. What do you think will happen?

(Professor – student conversation starts)

Student: It will expand the window.

Professor: Why?

Student: Krypton is a heavier gas.

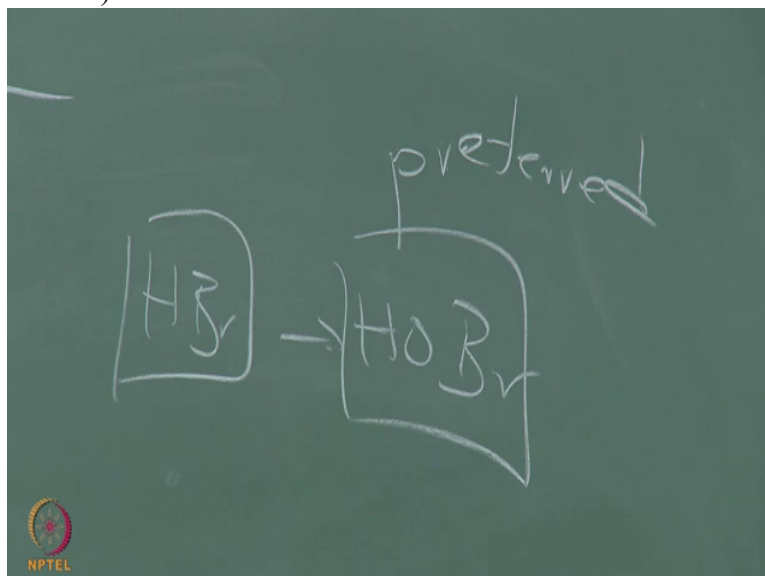
Professor: Exactly. So it will slow down the diffusion process. So you can operate in a wider window by using a heavier inert gas but more expensive, right?

(Professor – student conversation ends)

So again there may be cost economics that need to be taken into account but in general any species or any change in the process which slows down the diffusion process will certainly help you. And similarly with the fill gas you know, actually if you go from HBr let us say to hydrogen oxy bromide how do you think that will change things?

Will it again expand or shrink or, because this is a little more complicated because it obviously has to do with the reactivity of the species. Now when you use HOBr, it makes the system more reactive essentially. Now whether that is goodness or not, it is not easy to say a priori. But oxy bromides are preferred over HBr, can you think of a reason why we would prefer

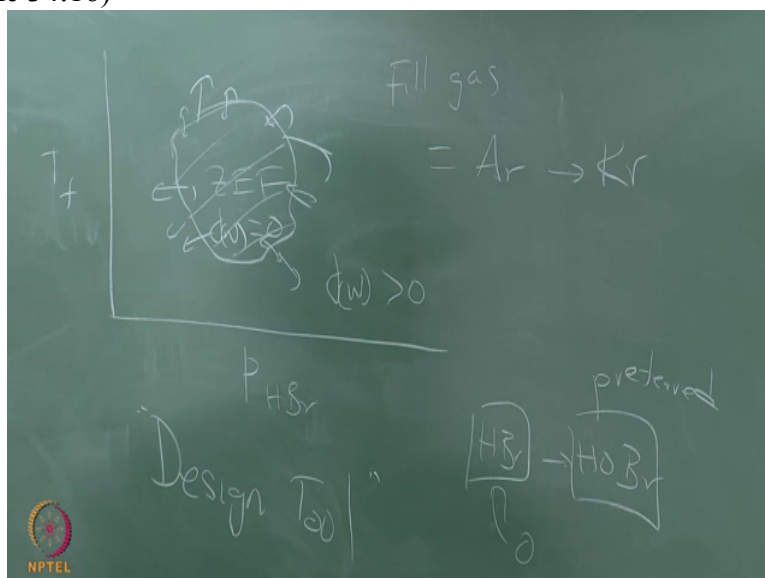
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to use an oxy bromide rather than a bromide?

See one simple reason is that we always have some trace oxygen. You know even if you have HBr as your gas that you have intentionally filled in, there is always going to be some leakage of atmospheric oxygen into the bulb. By providing the oxygen as part of your reactant molecule you have better control over it, right. So

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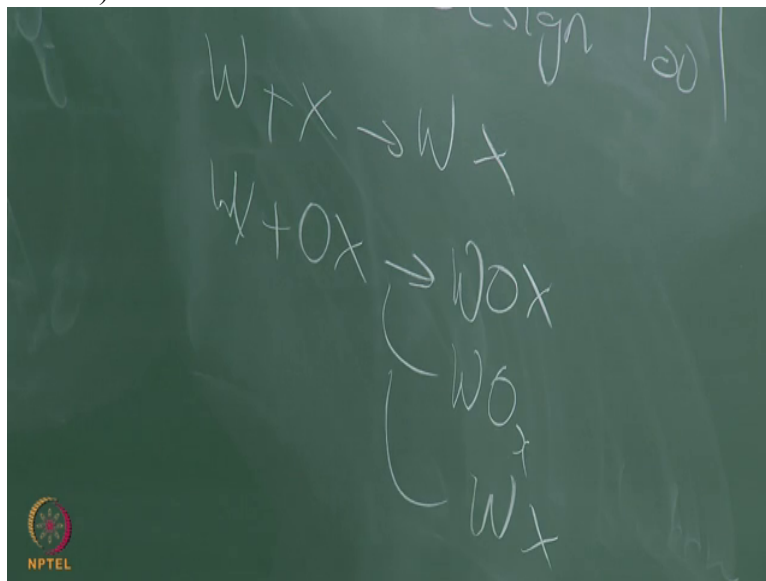


that is one reason why it is preferred.

The second reason is, see ultimately what you are trying to do is there is tungsten sitting on top of the bulb wall and you are trying to convert it to W_x . So a lot depends on how reactive that gas is with the tungsten that is coated on to the bulb.

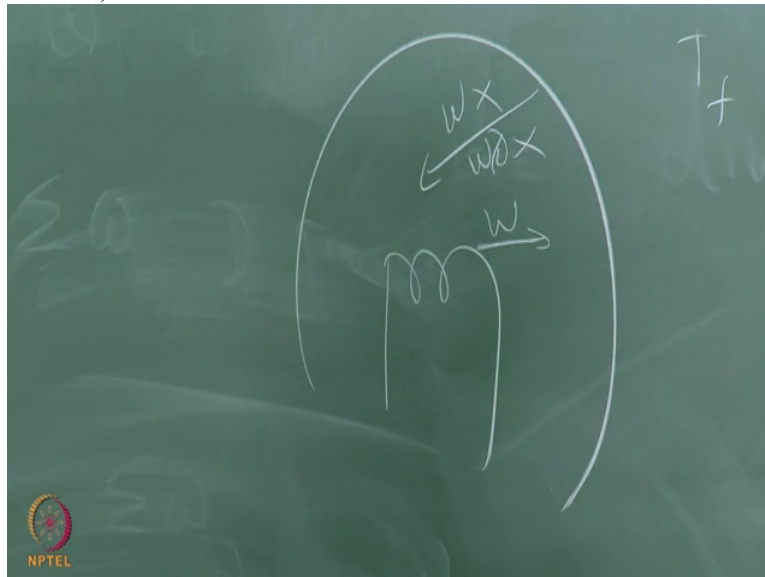
By having oxygen in the system you provide more opportunities to react with the tungsten and convert it into the gas phase. So if you have W plus O_x you can now produce more species. You can produce tungsten oxy bromide type of species, you can provide, you can produce $W O_x$ species and you can produce W_x species.

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So there are more ways in which the solid tungsten film on the bulb wall can be converted into a gas phase species that can then diffuse back. In terms of diffusivities as we discussed briefly in the last class, when you have the filament and the bulb, tungsten is diffusing this way and W_x or $W O_x$ is diffusing this way and the

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diffusivity scales with, scales inversely with size.

So the diffusion rate of tungsten back to the filament is always slower than the diffusion rate of tungsten away from the filament. And that is one reason why it is very unlikely that we will ever get a negative flux of tungsten. Tungsten flux will always be towards the bulb or zero. The best we can hope to achieve is zero.

Now when you introduce oxygen into the system, compared to W_x , $W O_x$ is going to be even slower because it is a, an even larger molecule. So what are the implications of that? It essentially means that if $W O_x$ is the only species that is produced, it is actually going to shrink the window, right? Because it is going to slow down the rate at which tungsten diffuses back to the filament. So this window will tend to shrink.

But because the presence of oxygen also allows the formation of $W O_x$ and of course W_x can still form, you are essentially negating that by providing more opportunities for tungsten to vaporize and get into the gas phase in the form of various species. So in general oxy bromides have found greater acceptance in the lighting industry compared to bromides.

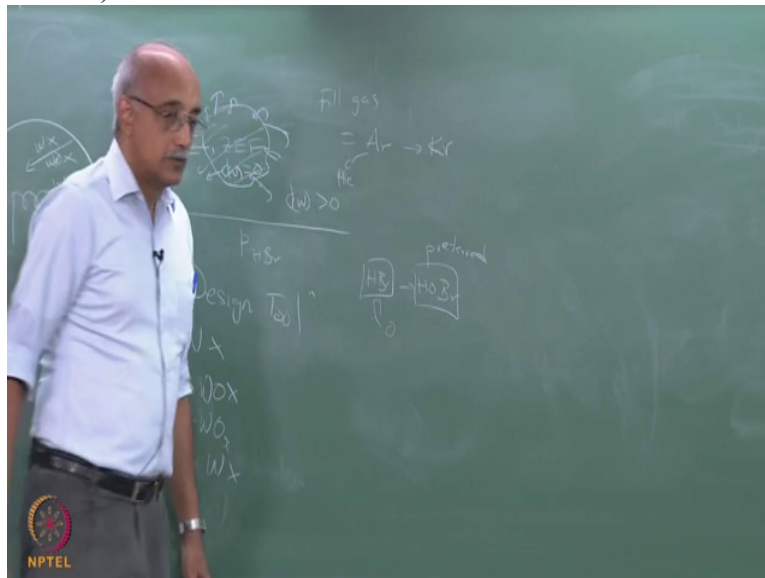
And by the way the other species like chlorides and so on have also been used but bromides are again considered optimal from the viewpoint of being able to produce the gas, fill the gas and obtain very repeatable and reproducible results. One of the problems with chlorine and fluorine, especially chlorine is that a, it is a corrosive material. So if you have impurities

present in the bulb environment, you can actually start seeing some evidence of chloride formation on the bulb wall. So in addition to forming tungsten, you may also start forming tungsten chloride type of deposits which you do not want.

And secondly because it is so reactive it is very difficult to control it in a sense. Even small variations in the concentration of chlorine at any one location can result in huge changes in the characteristics of what you find for the tungsten deposition. So a lot of interesting issues which have kind of resulted in the industry now predominantly using tungsten oxy bromide as the reactive gas and argon as the carrier gas.

Of course you can go the other way. I mean for example, if you use helium

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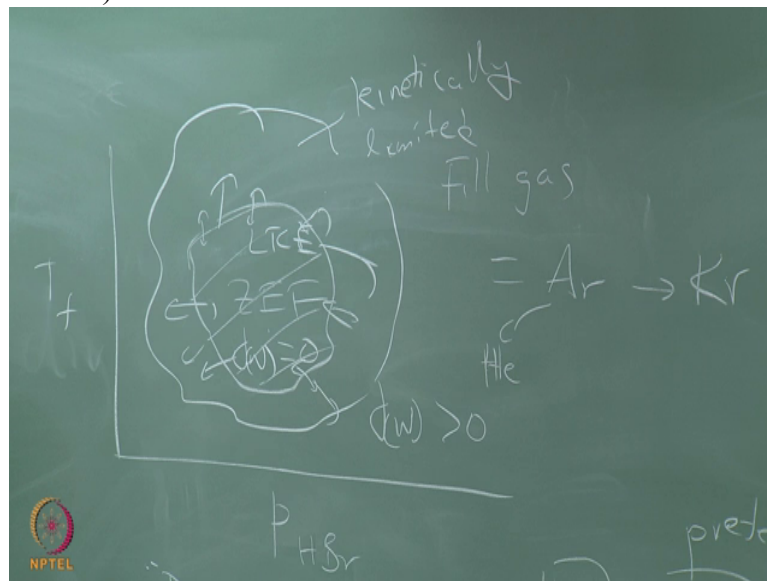
which is, which was, originally helium and neon were the species that were mostly used to fill the bulb but you can clearly see that because helium is a very light gas, the diffusivities will be extremely high. So your window of clean operation will shrink quite rapidly.

Now another way to look at this window is, so far we have been assuming as I said chemical equilibrium at the bulb. What if we relax that assumption and say that the reactions at the bulb will be kinetically constrained rather than going to equilibrium. What will that do to the window of zero flux? Will it make it smaller or bigger?

When we say that something is kinetically constrained what it means is the process is slowed down, right? So the process of formation of the tungsten film on the bulb surface will be slowed down when you have kinetic constraints. So this is kind of the worst case, the local thermo chemical equilibrium case.

The same window can be significantly enlarged if you assume that it is kinetically limited.

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But in terms of design you always want to provide the safety margin. So the design that assumes that every reaction will go to equilibrium will give you a significant safety factor and that is the reason why for design purposes people still continue to assume that the all chemical reactions will go to equilibrium even at the bulb surface temperature even though in reality they are significantly slowed down by the fact that the bulb wall is close to room temperature.

So, I mean, this is, you know multi-billion dollar industry even today when the fluorescent lamps are taking over from incandescent lamps, the ability to distinguish your product from the competitors, one of the factors is how long does it last? You know as a consumer that is the first thing that we look at.

You know if I buy this bulb will it last me for 1 year or 2 years? Will this other bulb, even though it is cheaper, if it turns to burn out at a shorter time, I am sure the consumer awareness

will build up around that and they will you know stop buying it and start buying something more expensive from the competitor.

We all do that and in fact the brand names like Philips, G E and so on have essentially built up consumer loyalty by focusing more on the lifetime of the bulb compared to just the purchase price. You can see a clear difference in how long a bulb from a branded manufacturer lasts compared to one from a non-branded manufacturer because, I mean they have research teams working on this kind of stuff.

G E has a research lab in Ohio which just focuses on lighting systems. And one of the key parameter they look at obviously is how to extend the lifetime of their lighting products in general. So it is worth paying the price for the extra technology, the extra understanding that these manufacturers have.

Ok so we will stop at this stage and in the next lecture we will take up another example of where C V D plays a very pivotal role in real life. Any questions on what we have covered today?

Ok see you at the next class