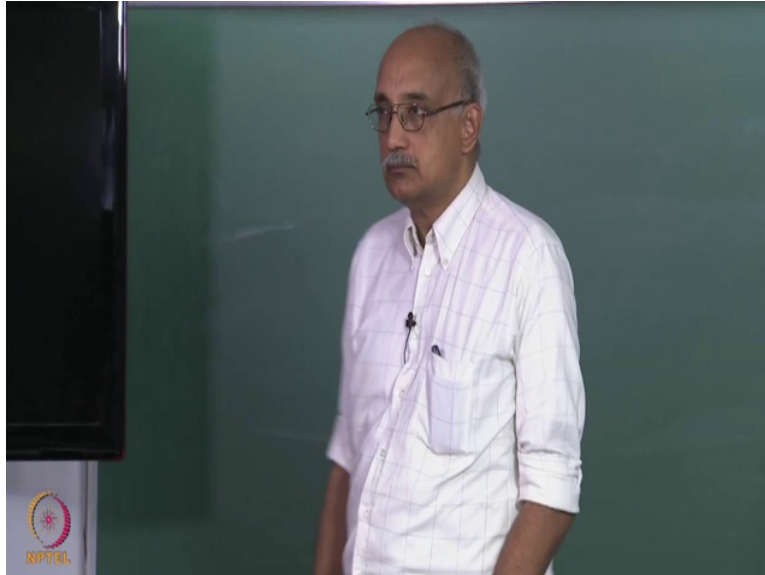


**Chemical Engineering Principle of C V D Processes**  
**Professor R. Nagrajan**  
**Department of Chemical Engineering**  
**Indian Institute of Technology Madras**  
**Lecture No 12**  
**C V D in Tungsten Filament Lamps**

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Good morning and welcome to the next lecture in our course on Chemical Engineering principles of C V D processes. In previous lectures in this course we have covered materials corresponding to the properties of C V D films, different types of C V D films and different structures, ways of analyzing film properties, various types of C V D reactors and operating conditions and so on.

From this lecture onwards we are going to focus more on the, the thermodynamic and transport aspects of C V D processes. And we will begin by looking at a couple of examples of C V D phenomena that we encounter in everyday life.

The first example is one that I referred to back in my first lecture which is the tungsten lamps, the tungsten filament's incandescent lamps that we use widely in our houses and other places. Although they are being increasingly replaced by fluorescent lamps and L E D lamps the incandescent lighting technology is still around and bulbs are not going to go away very soon. So how do these bulbs work? You know how do they provide illumination?

It is a very interesting application of C V D technology in the sense that they are actually using the C V D aspects of the bulb as a chemical reactor in order to extend its lifetime. So we will see what I mean by that. If you look at the history of lighting, basically lighting has been provided by incandescent sources from the beginning.

So if you look at the candle for example, or if you look at kerosene lamps or gas lamps, they all work on the same principle. You take some reacting gases and bring them to very high temperature and as you, as the temperature increases the solid particulates actually start glowing. And that is really what provides the illumination.

So all these early incandescent lamps worked on the principle of bringing these so-called soot particles to incandescence thereby providing lighting. The problem with these sources was that they were short-lived and they were highly polluting and they were creating an atmosphere where it was difficult to function.

So filament lamps were introduced. The first filament lamp was actually invented by Edison back in 1876 and that was a carbon filament lamp. Now carbon burns well and it provides good illumination but the problem with carbon is its vapor pressure is very high. So these carbon filament lamps, even though they worked quite well, their lifetime was the order of days.

Within days the bulb enclosure would completely get coated with carbon and become unusable. Now when you look at this from the viewpoint of a deposition process you have a carbon source and the film that is depositing is also carbon. So it is a classic example of a P V D process, right, physical vapor deposition process.

Now this problem was addressed in the early 1900s by adopting tungsten filaments instead of carbon. The advantage of tungsten is that it has about a 5000 times lower vapor pressure compared to carbon but it can also be brought to incandescence at a temperature that is fairly close to carbon filament.

The melting point of carbon is about 5000. The melting point of tungsten is about 4600 Kelvin. So the melting points are reasonably close, so you can heat them to very high, almost

as high a temperature as a carbon filament lamp but because of the lower vapor pressure now a tungsten filament bulb could be used for weeks instead of days.

So you are extending the lifetime by a factor of about 10 to a 100 by adopting a tungsten filament rather than a carbon filament. However it was still limited by the rate of evaporation of the tungsten. So sooner or later you will get this coating of tungsten around the bulb and therefore again you could not use it any more. So this is also a P V D process but a lower rate deposition process compared to carbon.

The next advancement in incandescent lighting technology came about when people originally, the carbon filament was being built in, was being burnt in vacuum. The, the next big advancement was to actually fill the bulb with an inert atmosphere with either inert gases or nitrogen thereby slowing down the rate of evaporation.

Now the way that works is when a filament evaporates the molecules leave the filament, get into the gas phase and then they diffuse and then they deposit on the, on the bulb around the filament. When you fill the bulb with some kind of gas, the gas molecules now actually can retard the motion of the tungsten vapor molecules

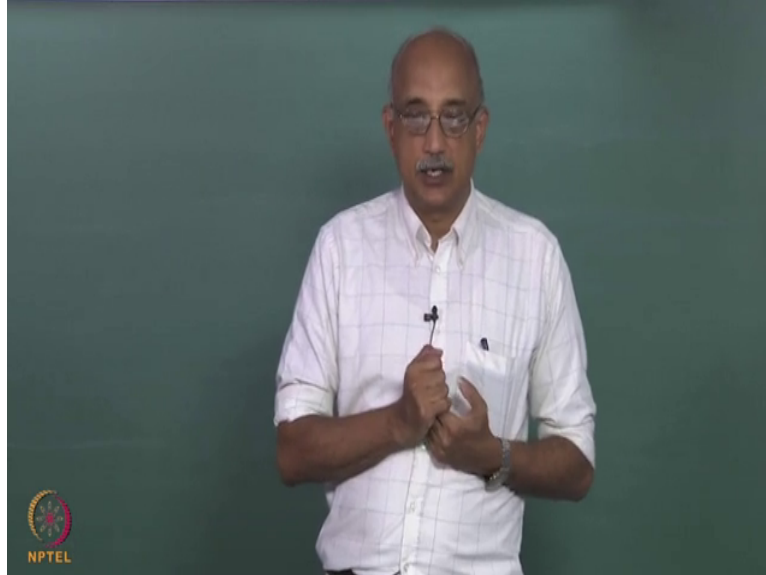
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and direct them back towards the filament.

So the net movement or the net flux of tungsten molecules towards the walls of the bulb is significantly

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reduced by the presence of this inert gas which provides the layer that, the vap/vapor, the tungsten molecules can bounce off of and return to the filament.

So the introduction of this inert atmosphere slowed down the onset of what is called as, what is known as bulb blackening which is the deposition of tungsten by another factor of I would say, around 10. So now instead of weeks a bulb could be used for months before it fails. But still within 5 to 6 months, these tungsten lamps with inert gas fillings would fail because the bulbs were coated with tungsten.

Now is this a P V D process or a C V D process? You have a tungsten filament that is burning, you have tungsten that is depositing, what form is the tungsten in in the vapor form inside the bulb? It is an inert atmosphere, right so there is no chemical reactions going on so the tungsten in the gas phase is also present as tungsten. So this is still a P V D process but slowed down even further.

So we went from having a carbon filament which had a very high vapor deposition rate to a tungsten filament which had a lower evaporation rate and therefore a deposition rate to a tungsten filament in a inert gas filled bulb which had an even further reduced rate of deposition of tungsten on the walls. But still it had a finite lifetime.

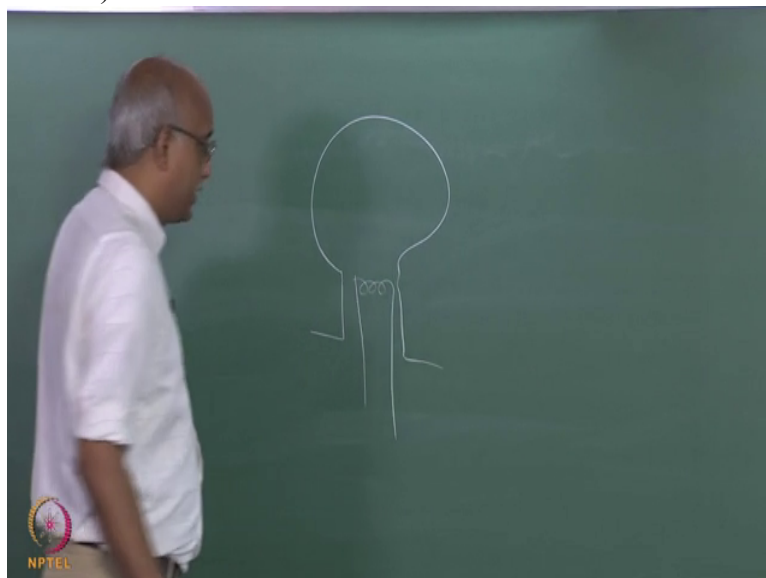
And it is still not economical for the industry. People were not happy of having to replace that bulb every four months. Now if you look at today, you know where we are still using bulbs what is the typical replacement frequency and why do we replace it? It can come for years, right? I mean usually these bulbs last, for you know couple of years and even after that they do not fail because tungsten has deposited around the bulb. They fail because the filament breaks.

So essentially this whole bulb blackening has now been eliminated as a mode for obsolescence of the bulb by some very, very clever design. So that is a big advancement. What made bulbs a viable industry was to introduce the halogens into the bulb. And achieve something called the halogen cycle.

So essentially we trans/transposed, transposed the bulb from having a P V D process to one having C V D process. So the way this works is when the tungsten evaporates from the bulb and gets into the gas phase, is there a way by which you can provide a flux of tungsten back towards the filament by having an appropriately reactive environment inside the bulb.

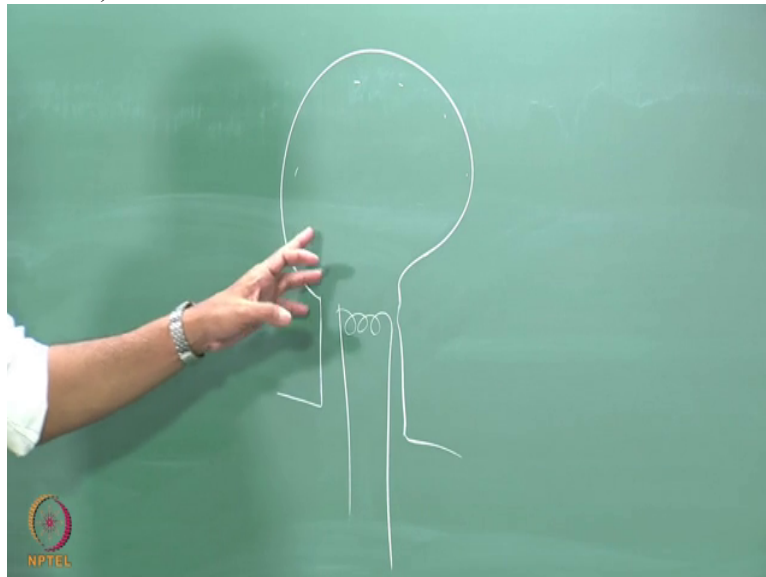
So if you think about it, again electric bulb,

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if you just look at it, it looks very much like a C V D reactor, right? It has a source and it has a sink. Of course the big difference here is that the

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substrate on which the deposition is happening is the walls of the reactor itself.

I mean if you can look at bulb as a reactor and the deposition of the evaporated material is happening around the walls of these reactor which is something we want to avoid in a, in a typical C V D reactor.

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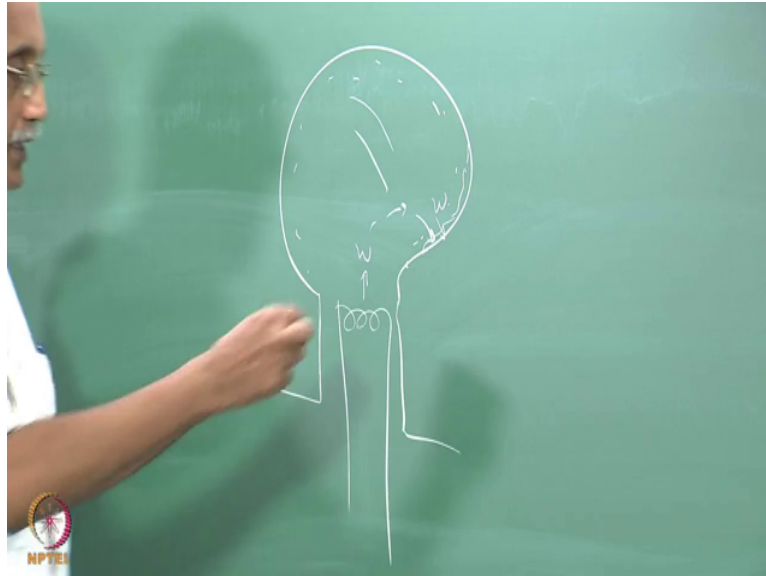
And that is the same case here.

What we are really trying to do is minimize or eliminate the rate at which the tungsten that is evaporated from here gets deposited on to the bulbs as a film. In fact later on we will talk about filament C V D reactors. They are designed exactly like a bulb except that they provide

flow of gases inside the, this reactor to take these vapors to a specified location so that essentially you convert an electrical bulb into a C V D reactor where the deposition is occurring over a well-defined substrate area.

But anyway coming back to the bulb situation then, so the problem is when tungsten evaporates it has a tendency to diffuse and deposit on the bulb walls.

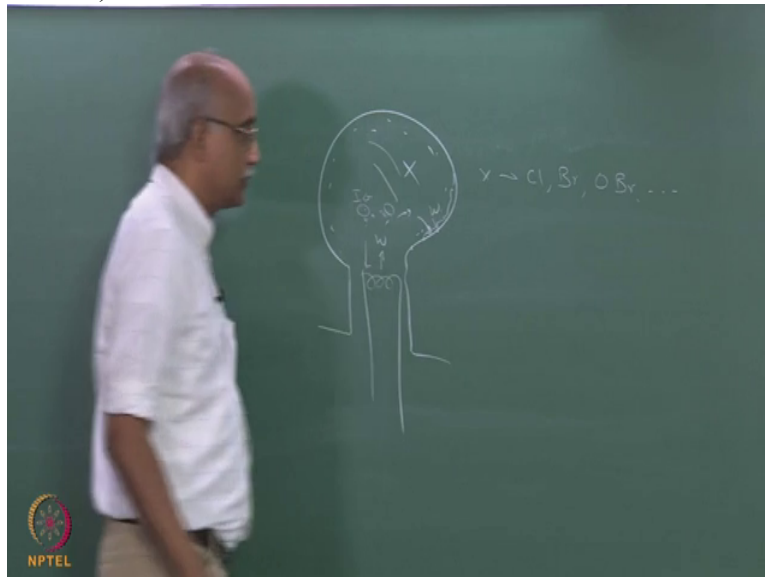
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And as I said, by providing these gas molecules inside, inert gas molecules, you can, because of the collision between the vapor, tungsten vapor molecules and the inert gas molecules, you can direct some of the tungsten vapor molecules back towards the filament and thereby slow down the rate of deposition.

But the major revolutionary change that happened was introducing halogens  $x$  where  $x$  could be Cl, Br; it could even be oxybromides and so on

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into the bulb before it is sealed up. How does that help you? Well, when you look at this area, suppose the tungsten film starts to deposit but you have a reactive material

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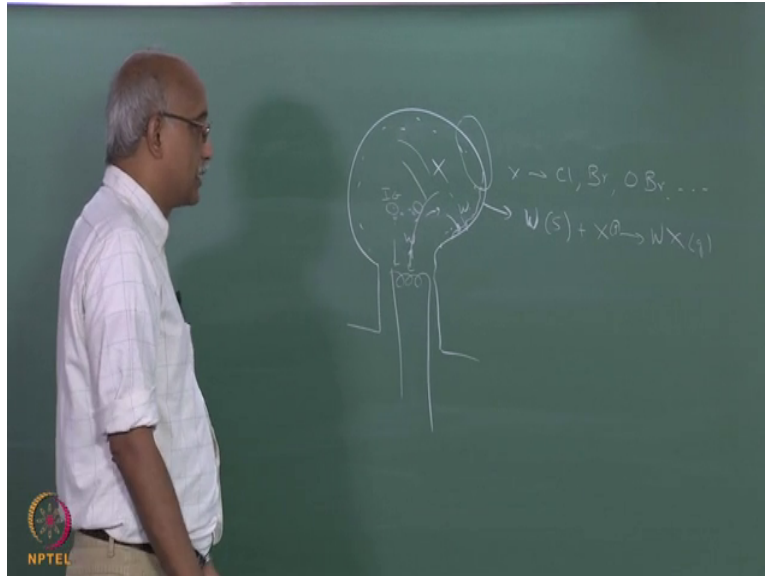
like Br present.

The tungsten is going to react with the Br and get converted to tungsten bromide. And stay in the gas phase. So the reaction that occurs here is W solid plus x going to W x. So this is in the gas phase and this is in the gas phase. So what will this W x do once it is formed? It has the tendency to diffuse back to the filament because it follows Fick Diffusion.



And Fick diffusion says diffusion occurs down a concentration gradient. Since there is an excess of  $Wx$  concentration near the walls of the bulb and there is virtually no  $Wx$  at the filament, the  $Wx$  will diffuse back towards to the filament.

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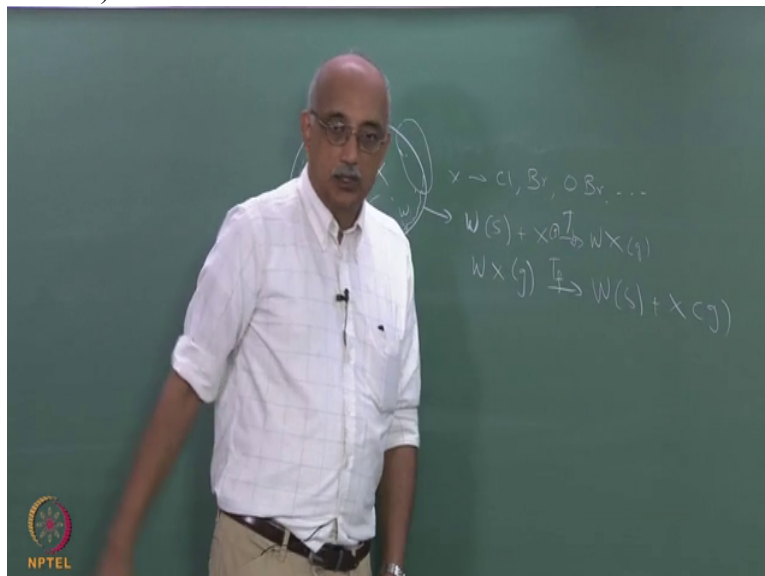


And what will happen?

When it gets to the filament  $Wx$  gas at the temperature of the filament, let us call that some  $T_f$  and this is happening at the temperature of the bulb, let us call that  $T_b$ , this  $Wx$  gas breaks down into  $W$  solid plus  $x$  gas.

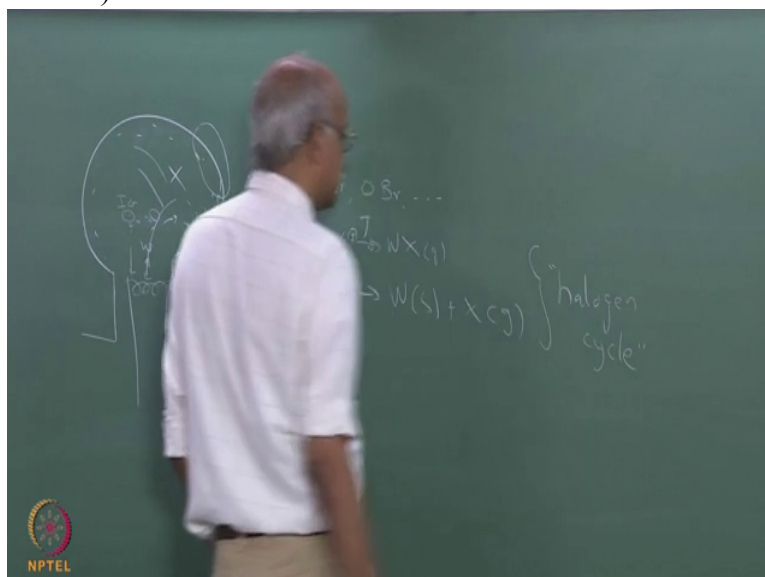
So it releases this  $x$  gas back into

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the gaseous environment. The tungsten itself is re-deposited on to the film in the form of solid tungsten. So this is essentially a cycle, right, and it is known as the halogen cycle.

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So if you look at this halogen cycle, in principle it can be set up so that the rate at which the tungsten is evaporating from the filament is exactly balanced by the rate at which it is getting replenished by suitably balancing the rates of transport of the corresponding molecules.

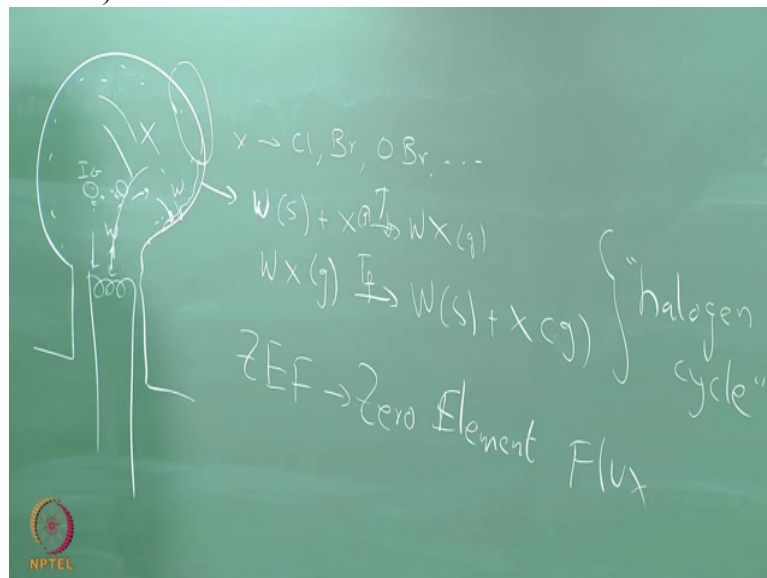
So that is a clever concept behind the halogen cycle. Now in principle this bulb can have an infinite lifetime. It will keep going as long as this cycle is present. And in fact that is what is exactly happening today in the bulbs that are manufactured. They all have a halogen

environment and that is the reason why they are not failing anymore because of a simple film deposition process.

So it is a classic example of the C V D reaction that is very elegantly set up in order to achieve a certain purpose. But it is very different of course from the commercial C V D applications that we have talked about so far. But it actually illustrates the principles quite well in terms of what is happening inside this, whether you call it a bulb or a reactor, you know, there is a C V D process is actually happening inside here.

So how do you provide this balance? I mean there is something called a Z E F which stands for zero element flux. This is the condition you are trying to achieve.

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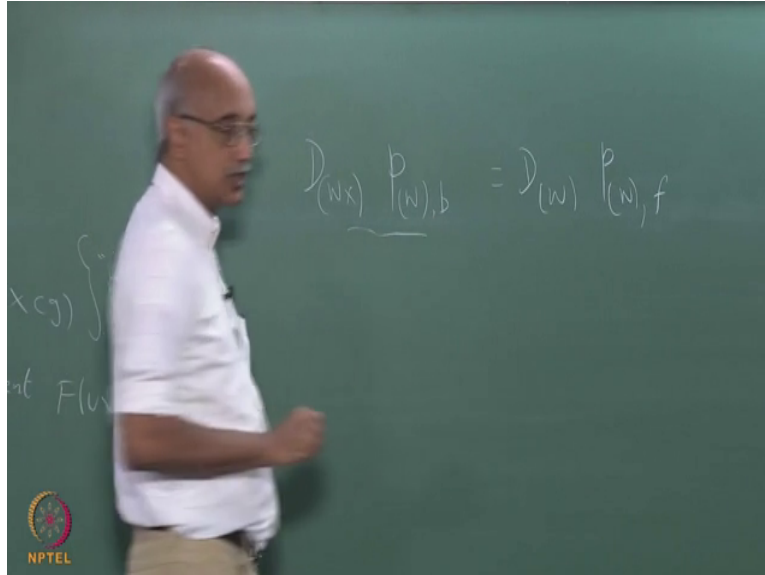
You want zero net flux of the element in this case is tungsten. You want the evaporative flux of tungsten to be exactly balanced by the re-depositing flux of tungsten so that the net is zero. So how do you achieve this? In order for this to happen, the flux that is leaving the filament must be balanced by the flux that is re-depositing or getting re-transported towards the filament. An easy way to think about it is in terms of diffusivities. So you have  $D_{Wx}$  which is the diffusivity of the gaseous species  $Wx$ , that multiplied by  $P_W$  at the bulb wall must be equal to  $D_W$  times  $P_W$ .

It is basically a diffusional mass balance. It basically says that if you take the partial pressure of tungsten near the bulb and you multiply it by the diffusivity of the dominant species

containing W that should be exactly equal to the diffusivity of tungsten vapor species near the filament multiplied by the partial pressure of tungsten near the filament.

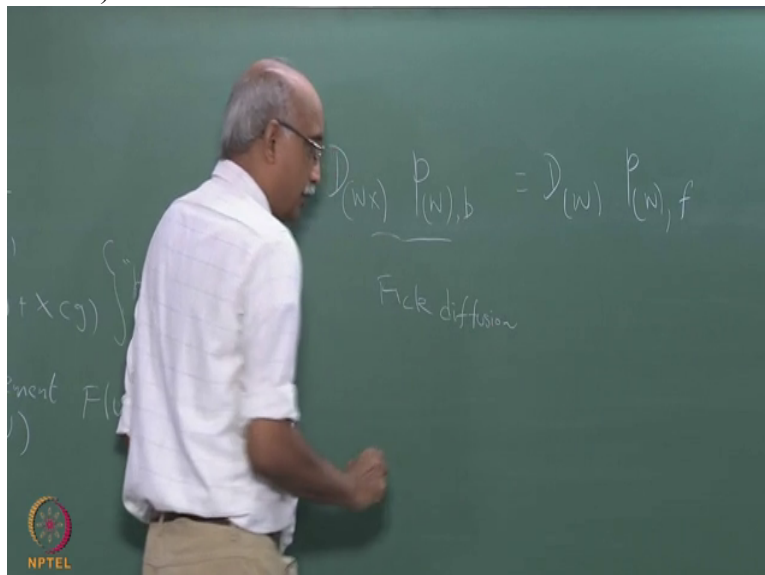
These are essentially mass fluxes written in terms of partial pressure

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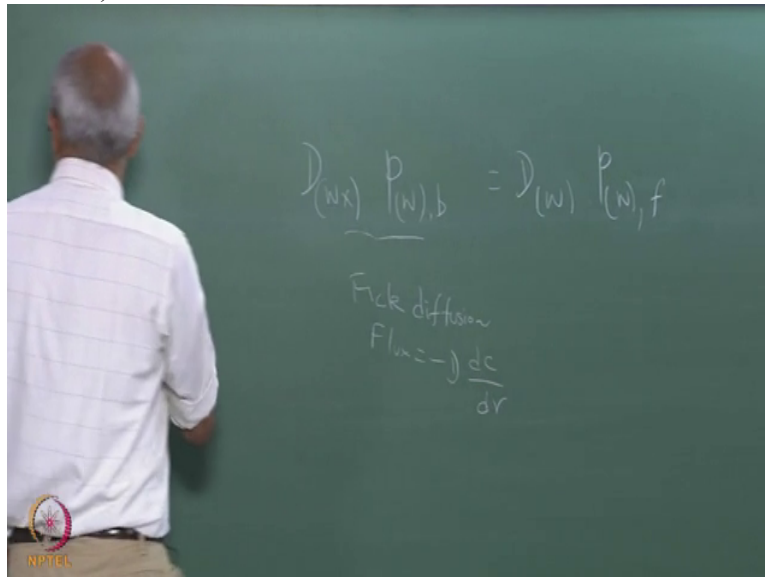
instead of concentration but it is the same, I mean basically these are the Fick diffusion fluxes.

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Normally you would write Fick diffusion flux as some minus  $D \frac{dc}{dr}$  in this case,

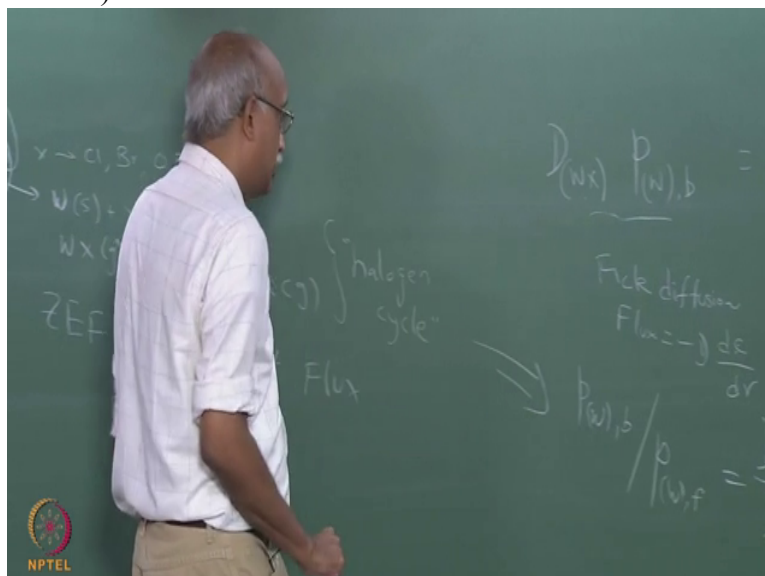
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assuming it is a radial symmetry. That is basically what we have written here except that the  $d$  in this case is basically equal to the partial pressure on one side because the partial pressure on the other side is virtually zero, right.

That is where this equation came from. So if your partial pressures  $P_{W,b}$  over  $P_{W,f}$  is exactly equal to the ratio of the diffusivities which is  $D_{W}$  over  $d_{Wx}$  this is called the

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zero element flux condition. If the partial pressures are exactly in this ratio, in the ratio of their diffusivities, then there will be no net flux of tungsten either way.

It will be in dynamic balance, not static, it is an equilibrium dynamic balance. So if you can design your bulb in such a way that you achieve this balance then it will operate forever in principle. Now if you look at that ratio  $D W$  by  $D W x$ , is it greater than 1 or smaller than 1?

(Professor – student conversation starts)

Student: Less than

Professor: Why is that?

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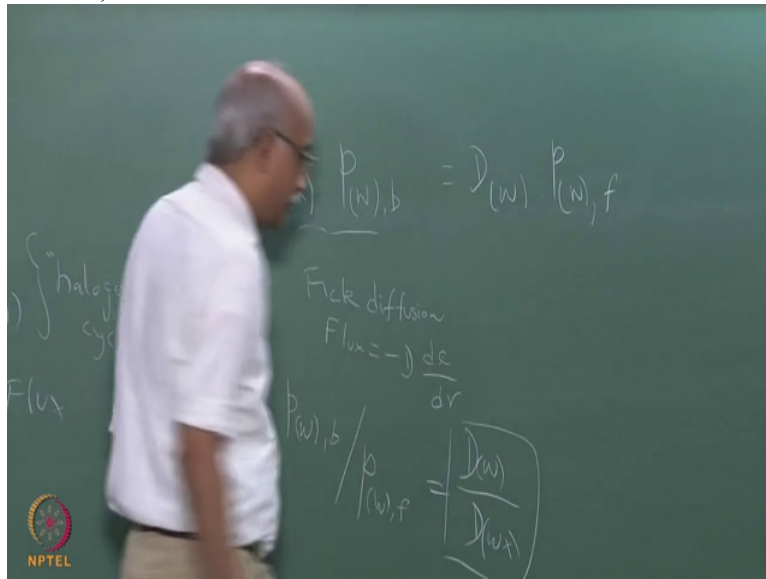
Student: Greater than 1

Professor: Why is that?

Student: Partial pressure in bulb will be higher.

Professor: No, just look at the right hand side. I am just looking at this ratio,

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$D_W$  over  $D_{Wx}$ . You have two molecules, one is the tungsten molecule, the other is the tungsten halide molecule. If you look at the ratio of diffusivities, will it be greater than 1 or smaller than 1?

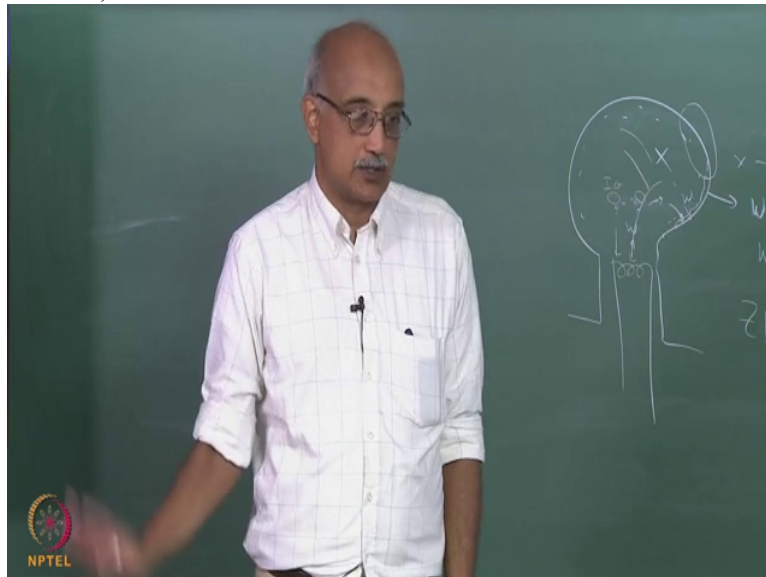
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Student: Gas diffusivity will be...

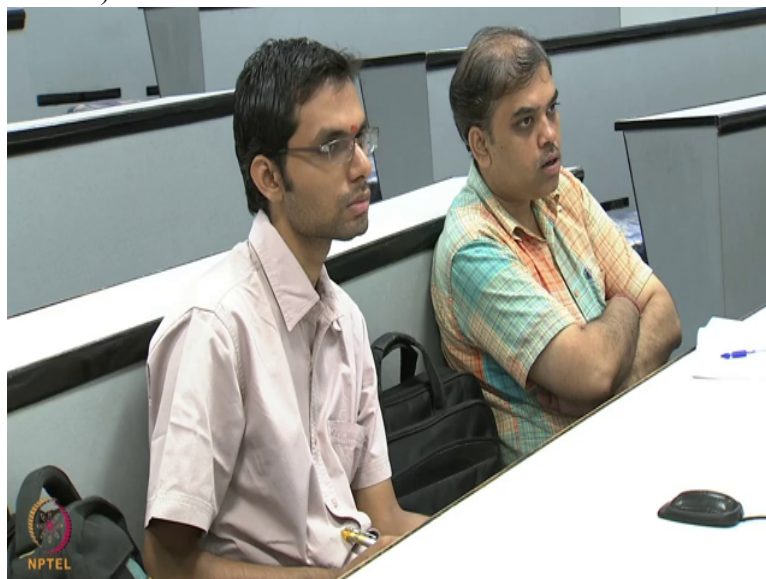
Professor: They are all in

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gas phase. W is also in gas phase, W x is also in gas phase.

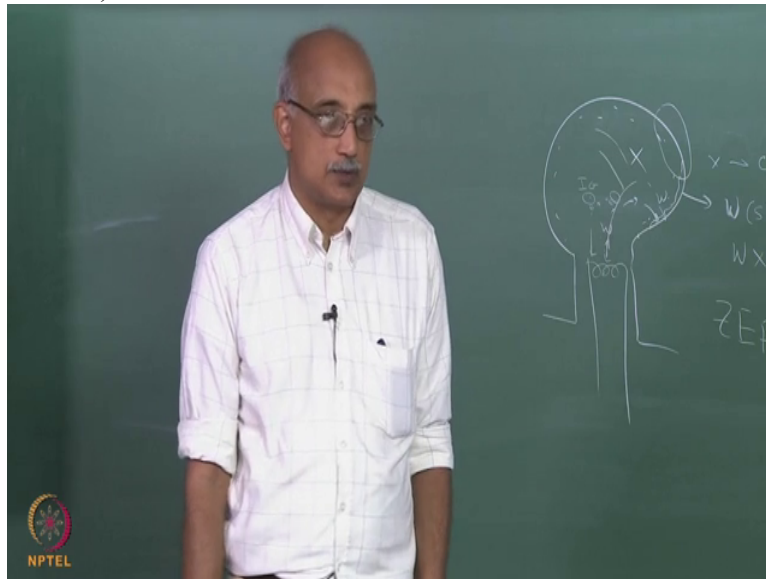
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These are all gas phase molecules, right? The diffusion process we are talking about is all happening in the gas phase. Solids do not diffuse.



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Student: The molecular weight of

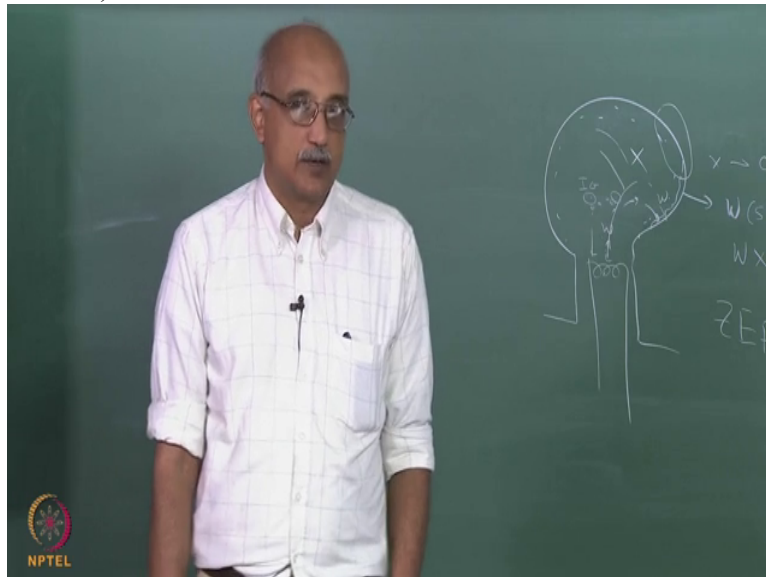
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$w_x$  is higher. So diffusivity will be affected by the molecular weight.

Professor: It is not

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the molecular weight but yeah so?

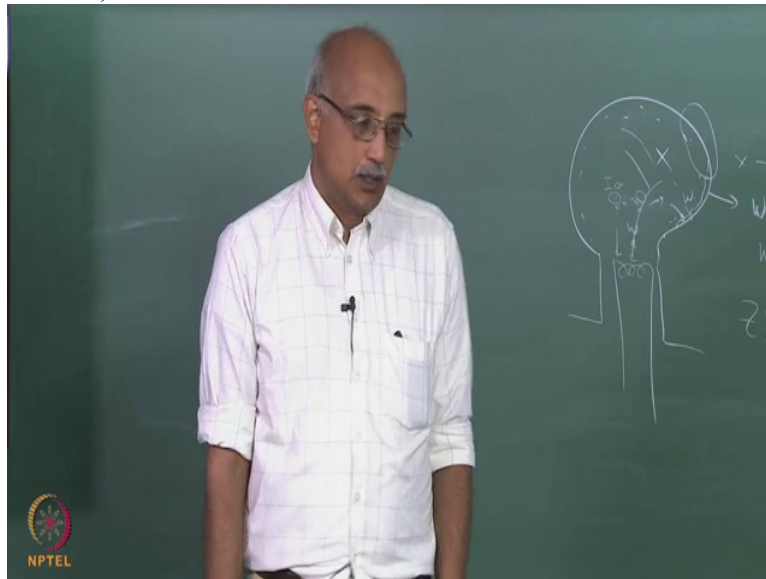
Student: So  $D W x$

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will be greater than  $D W$ .

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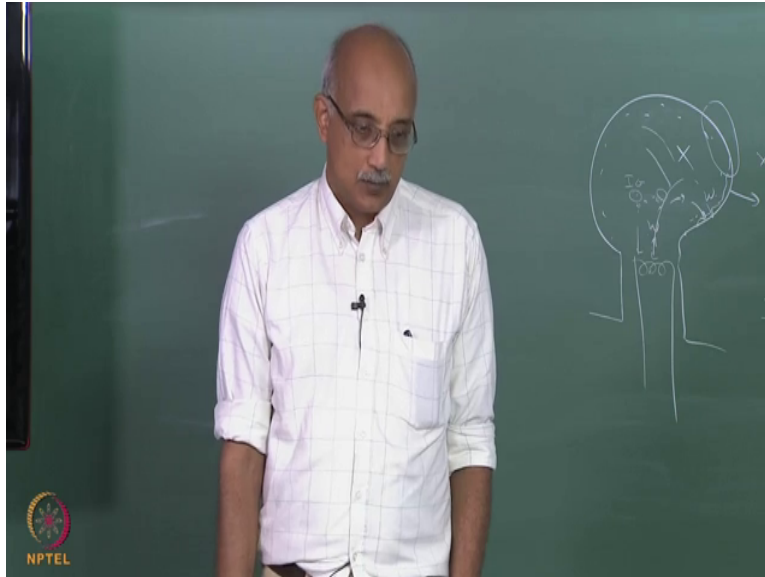
Professor: It is exactly the size. Which one will be larger, will  $W$  be larger or  $W x$ ?

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Student:  $W x$

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Professor: And as size increases what happens to diffusivity?

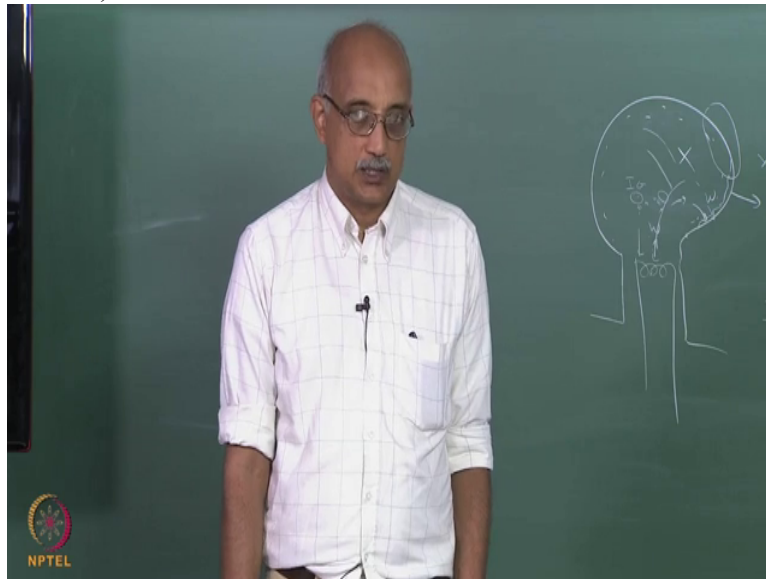
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Student: Reduces

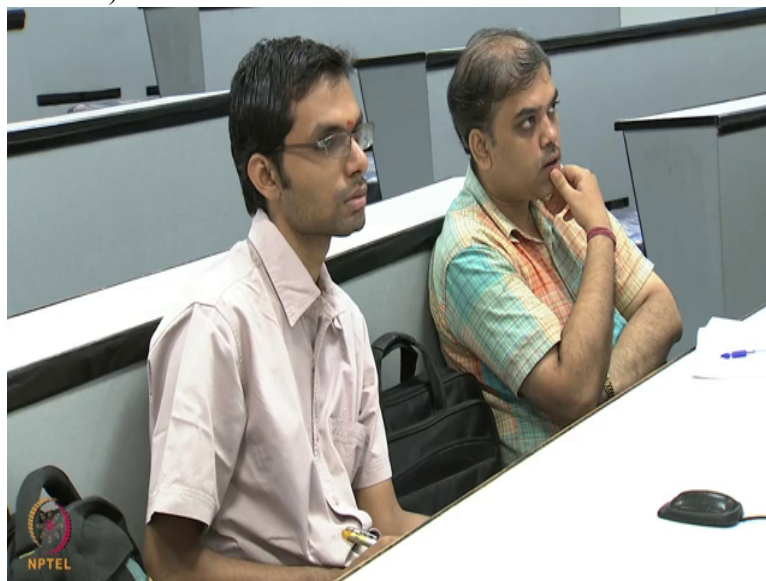
Professor: So which one is

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lower in this case?

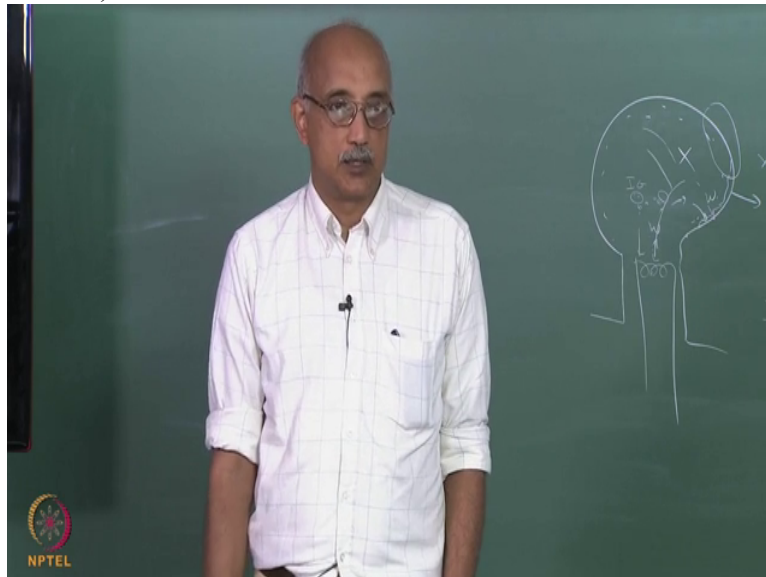
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Student: D W x

Professor: So this ratio is always greater than 1.

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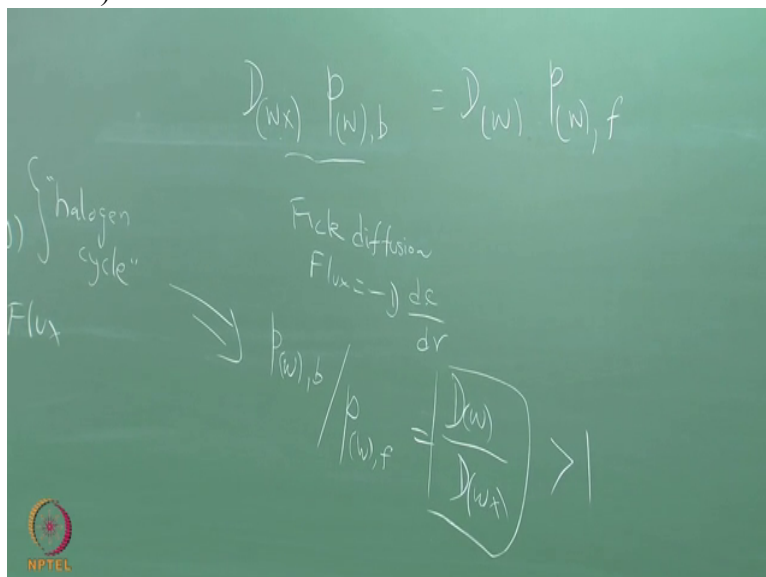


Diffusivity of a tungsten halide molecule is always lower than the diffusivity of the tungsten molecule. So this ratio is always greater than 1.

(Professor – student conversation ends)

If the tungsten pressure,

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partial pressure at the bulb exceeds this value, this particular ratio then what happens? You get more deposition back towards the filament, right in order to achieve balance again. And similarly if this becomes larger then what happens? You get more transport towards the bulb.

Now, so what happens today when bulbs fail? Why do they fail? Because there is a sudden increase in this value. And why does this happen? When a filament breaks, the area that is exposed is suddenly much larger. So the rate of evaporation is much greater.

So there is an instantaneous jump in the partial pressure of tungsten in the gas phase that is adjacent to the hot filament. And therefore you have a sudden shift in the equilibrium and all of a sudden the bulb becomes very black. You know, you will see that as soon as the filament breaks the entire bulb will look black, right? And that is the reason.

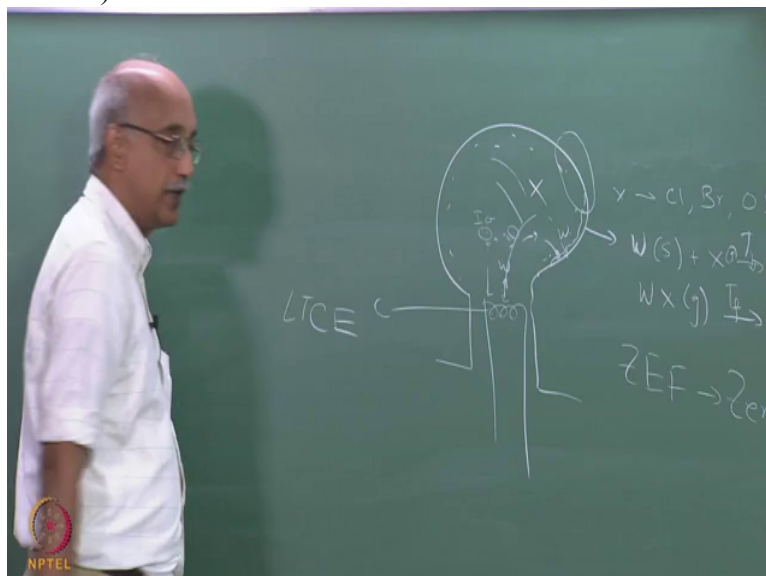
So very basically, this is how a bulb works and as long as you can maintain the zero element flux condition inside the bulb, it will be in good shape. But as soon as you break the condition, there is a tendency for it to fail for one reason or the other.

Now if you do a transport analysis, this what I have shown here is a very simplistic way of looking way of looking at it but you can do a more rigorous transport analysis of the system as well as the thermodynamic analysis of the system.

In terms of thermodynamics, because the filament temperatures are very high, you know 4000 Kelvin somewhat in that range, the assumption of local thermo chemical equilibrium is valid. The higher the temperature the more the closer you get to equilibrium conditions.

So active filament, you can assume that what is known as L T C E prevails.

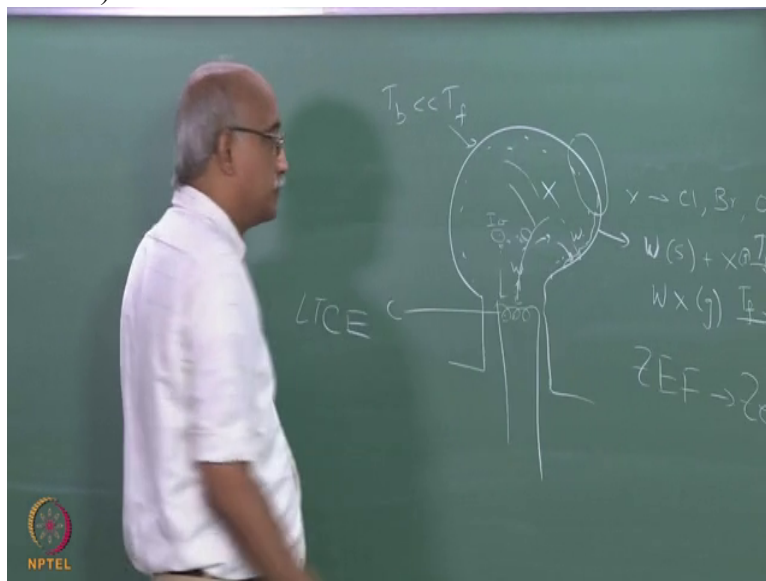
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L T C E stands for local thermo chemical equilibrium. So you can calculate your gas phase composition by using, for example the free energy minimization procedure that we discussed earlier in class. The assumption of chemical equilibrium is valid at the filament and close to the filament.

But if you look at the bulb wall, the outer wall is at room temperature, right? The inner wall gets heated up because of the radiation from the filament but still this  $T_b$  is going to be much smaller than  $T_f$ .

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So given that is it still Ok to assume equilibrium at the bulb wall or it is going to be kinetically constrained.

Well, strictly speaking, yes you would have kinetic constraints that come into play because temperatures are not high enough to guarantee equilibrium conditions. But there is a gradient. The temperature changes gradually from  $T_f$  to  $T_b$  inside the bulb so at each prevailing temperature you have to reassess the validity of the equilibrium assumption.

Is the equilibrium assumption only valid near the filament? Is it valid till about halfway across the bulb or is it valid all the way up to the bulb wall? That is a very important consideration in terms of the thermodynamic analysis.



Because if you can assume chemical equilibrium throughout the bulb, then it becomes fairly straightforward to calculate the composition of gas phase inside the bulb simply by assuming free energy minimization strategies; however if you have to assume kinetic constraints then you have to really understand the dominant chemical reactions that are taking place inside the bulb.

So it requires a lot more analysis. It requires a lot more monitoring. And so if I am a bulb designer I will try to operate the bulb in such a way that I maintain equilibrium conditions as much as possible inside the bulb.

Now in terms of transport, what happens inside the bulb? You have a heated filament and you have a sealed enclosure. What kind of flow do you expect inside this enclosure? Will you have turbulent flow, will you have laminar flow, will you have unidirectional flow, will you have recirculating flow or will you have no flow? What do you expect? What are the types of fluid flow that can happen?

There is, let us say, in terms of, let us talk about heat. You know, we are essentially transmitting the heat from the filament to the bulb. What are the mechanisms of heat transfer that can happen? There is conduction, convection and radiation, right?

Conduction will certainly happen, as long you have a hot source and there is a temperature gradient. Radiation will happen because it is a, you know radiating source that is at a very high temperature. How about convection? Can convection happen inside a bulb?

(Professor – student conversation starts)

Student: 0:24:56.3 temperature difference

Professor: So there will be natural convection, right?

Student: Natural convection

Professor: So in principle, all three modes of transport can happen.

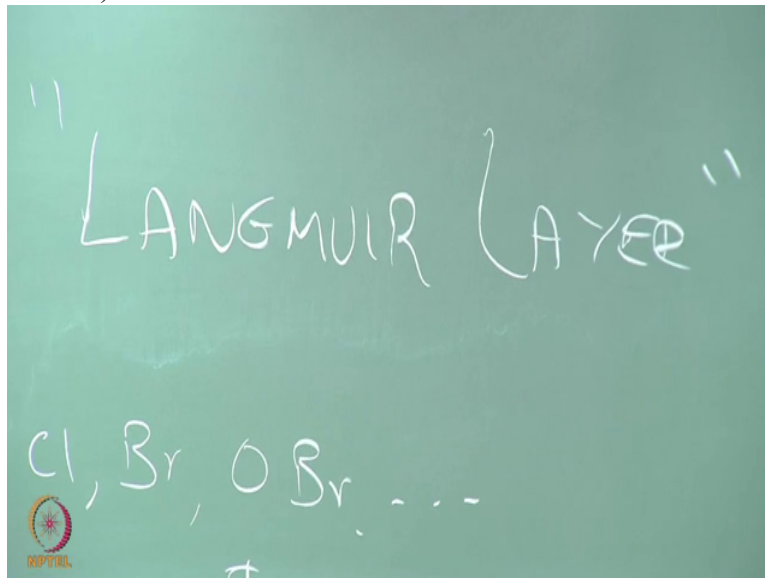
(Professor – student conversation ends)

However in terms of the convection part, again if I am a bulb designer, I want to design it so that the entire fluid region inside the bulb is stagnant and there is no flow. The reason is as soon as you set up a flow, it increases the rate of mass transfer.

So if the filament starts to evaporate the rate at which these molecules will be transported away from the filament and deposit on the bulb will be greatly enhanced if there is natural convection going on. So you want to design the bulb in such a way that there is stagnant layer inside the bulb with no natural convection and the stagnant layer extends all the way to the walls of the bulb.

This type of layer is called the Langmuir layer. Within a Langmuir

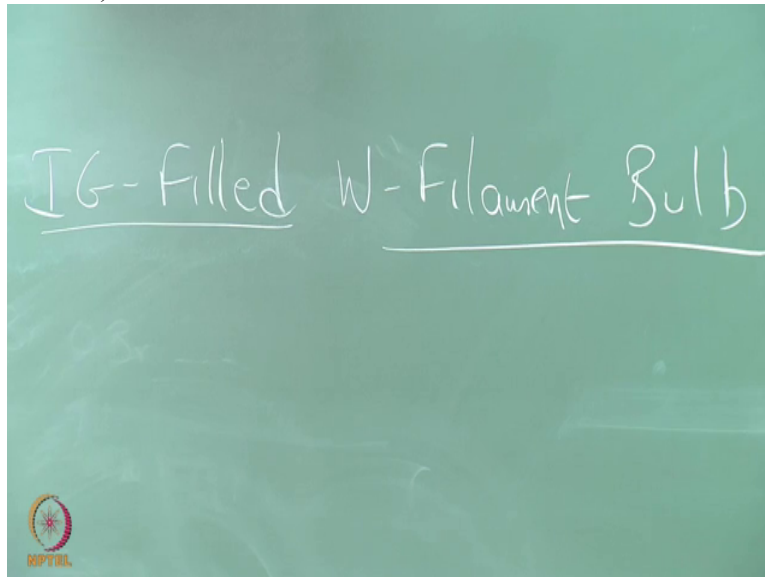
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layer surrounding an object the only modes of transport are conduction for energy and diffusion for mass and momentum. Under these conditions the rate of loss of tungsten from the filament can be greatly minimized.

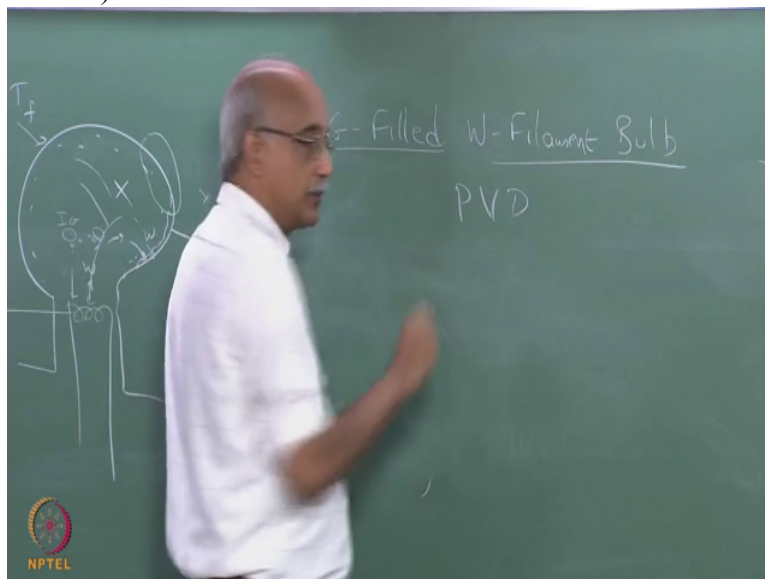
So as a design principle you would want this Langmuir layer to extend all the way from the filament to the walls of the bulb. So let us say that you have achieved Langmuir conditions. And let us say that you are operating this tungsten lamp under conditions where you have only an inert gas inside the bulb. So we are looking at the case of an inert gas-filled tungsten filament bulb.

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So essentially the deposition process that is going on is a P V D

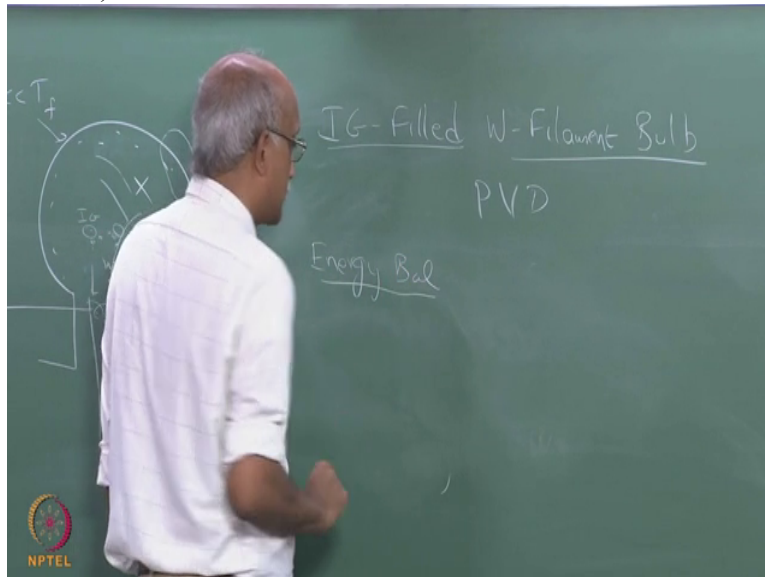
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process. The tungsten that evaporates from the filament stays as tungsten. So it just goes from being solid phase tungsten to being gas phase tungsten and then at the walls of the bulb it redeposits as solid phase tungsten, right?

How would you do the transport analysis of this type of a problem? The first you have to write the energy balance.

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How do you write conservation equations? How many terms are there in a typical conservation equation, for mass, momentum, energy, entropy what are the four...how many terms and what are they?

(Professor – student conversation starts)

Student: Four terms

Professor: Yeah

Student: 0:28:04.6 accumulation, inflow, outflow and generation

Professor: Ok,

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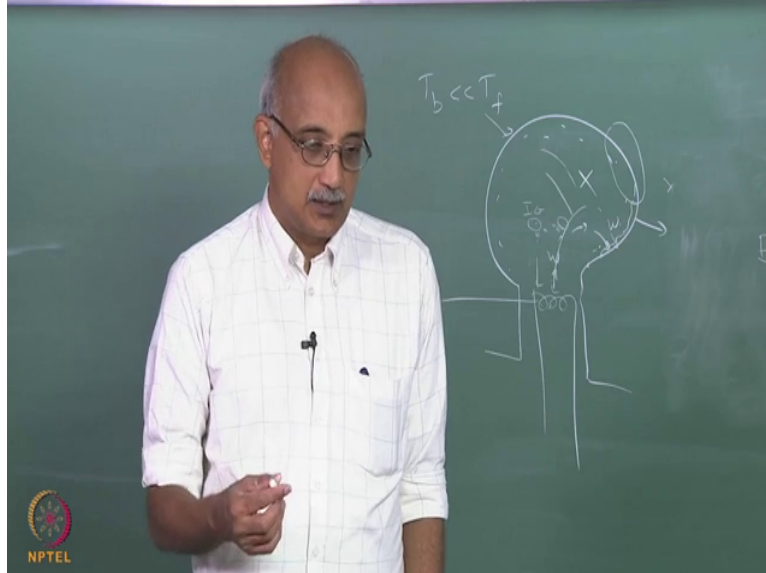


inflow is by what mechanism?

Student: If there is any, anything comes from outside, flow of energy from outside.

Professor: Ok, but we just said these

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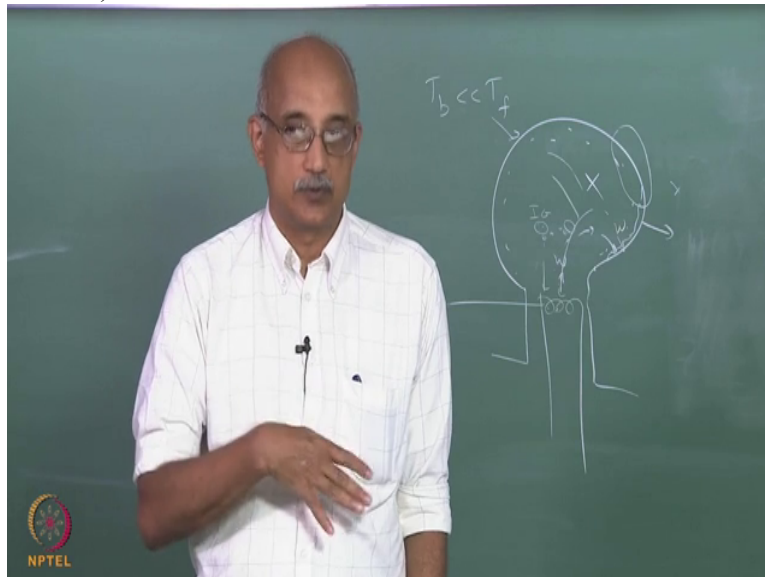
three modes of transport, right, there is convection, diffusion, so when you write a mass balance, or a heat balance, you have to say it in terms of, accumulation is one, generation is another, but then there is

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flow but conventionally it is split into convective outflow and

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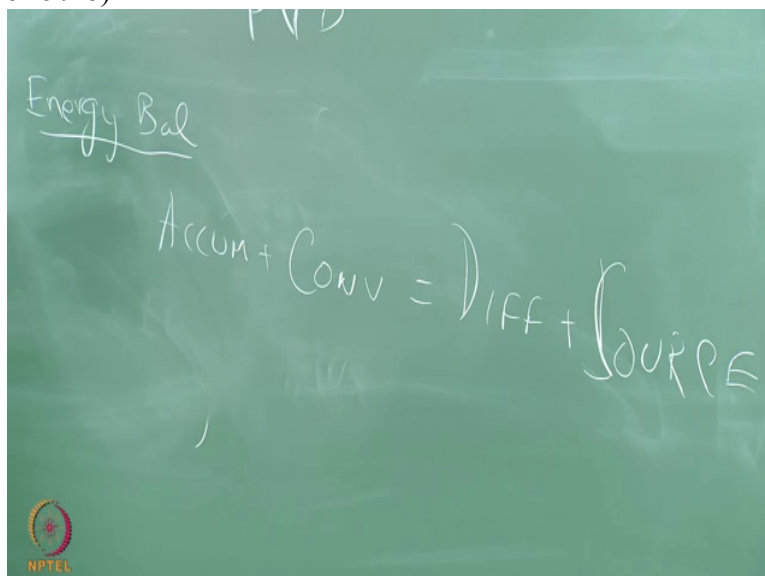
diffusive inflow.

(Professor – student conversation ends)

So essentially any energy balance or any kind of balance equation is written in terms of accumulation term plus a convective term which balances a diffusive term plus a source or sink term, right? That is a general formulation of a conservation equation.

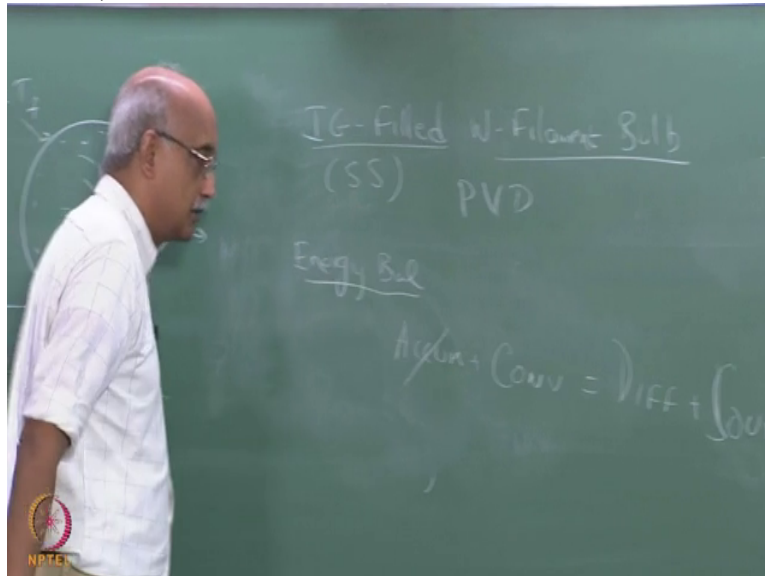
So in the specific case of the inert gas-filled tungsten filament

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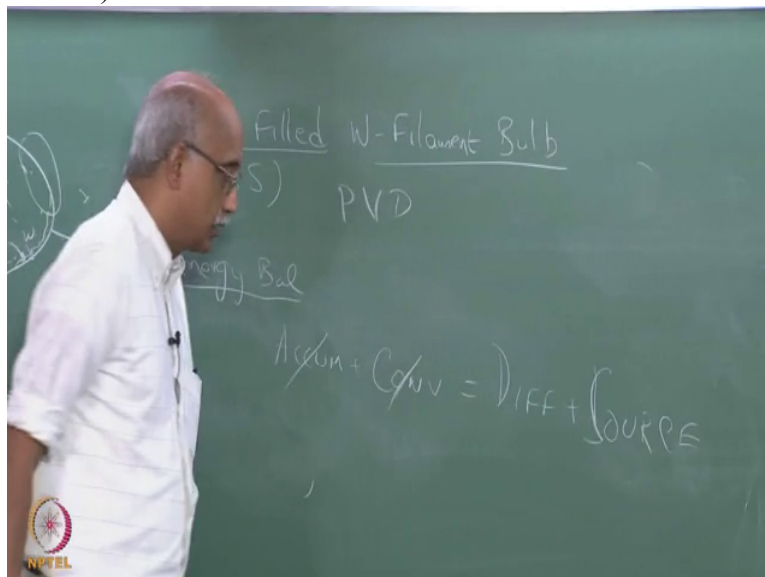
bulb, let us say that you are doing a steady state analysis, Ok. So the accumulation term drops. So you are assuming that it is under

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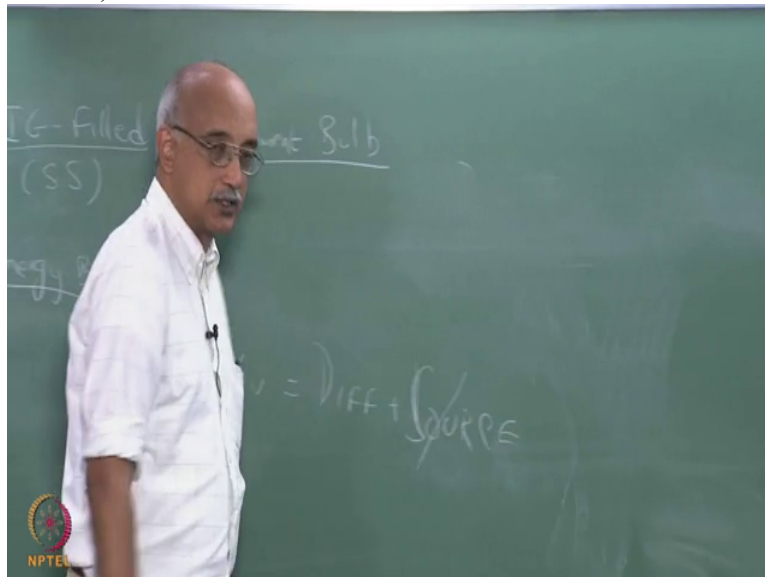
steady state conditions. Convection, we just said, we will design it so that there is no convection inside the bulb so this term will drop.

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The source term for heat, that is radiation but again once you have achieved a steady state, the radiation term is not going to really affect your heat flux

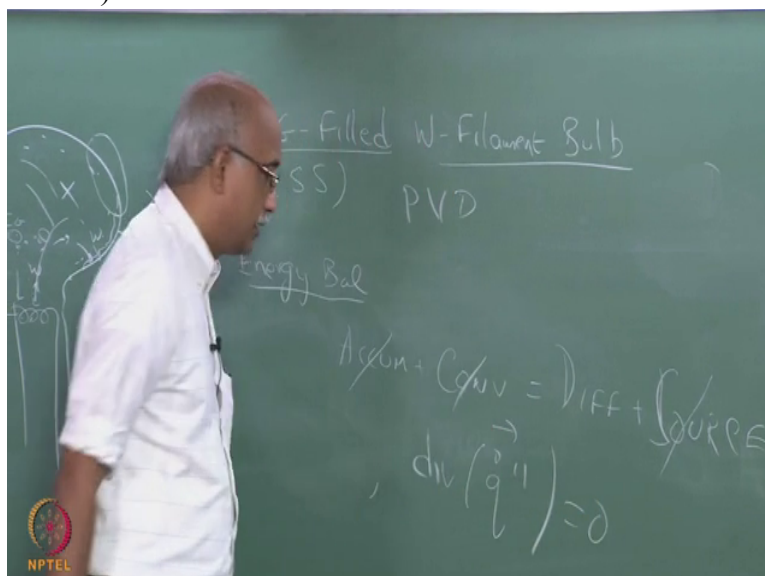
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in terms of the time-dependent change or the position-dependent change in your temperature distribution for example. So essentially you just have to solve the diffusion equation to know the temperature distribution inside the bulb.

And that is done in terms of a divergence, a divergence of,

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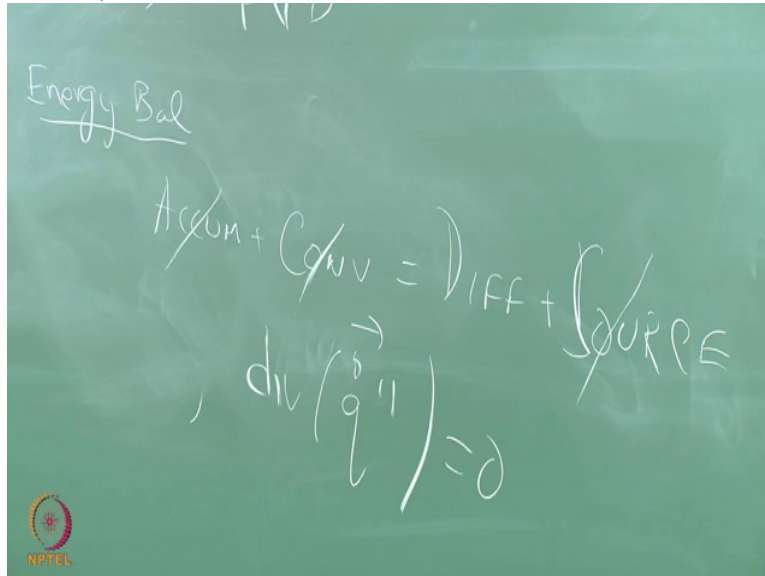


divergence of heat flux equal to zero. You know divergence, right? You have gone through this in your heat transfer course. So the notation that I am using here is the dot on top stands for per unit time and this double prime stands for per unit area.



So what this equation means is it is a divergence of the heat flux which is expressed as heat transfer per unit time per unit area; that must be equal to zero. Right, that is a

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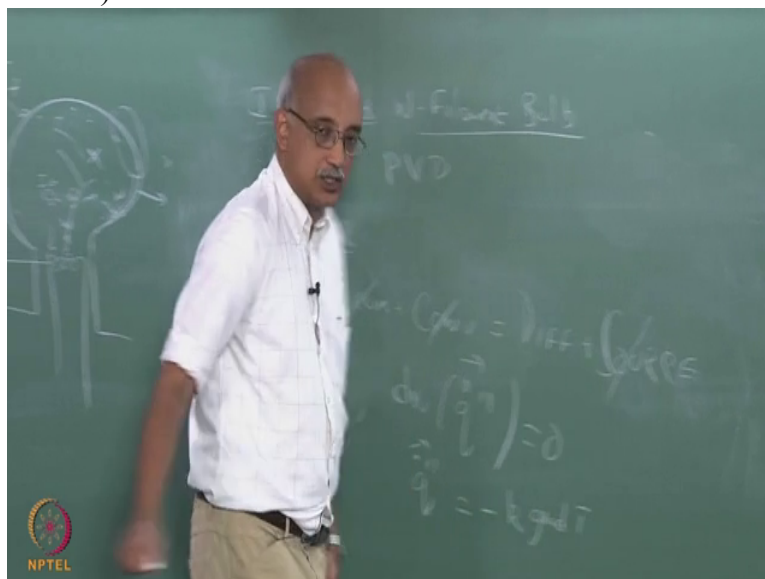
diffusion equation in its simplest form where this  $q$  dot double prime can be written in terms of, if this is a conduction term, how do you write  $q$  dot double prime? What is....?

(Professor – student conversation starts)

Student:  $k \frac{dT}{dx}$  minus  $k \frac{dT}{dx}$

Professor: Minus  $k$  times gradient

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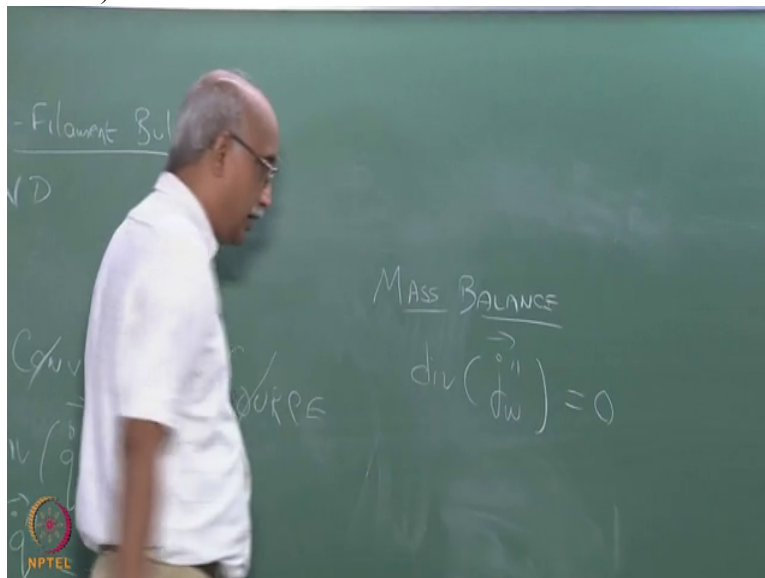


in temperature, right? What is the corresponding mass balance? How would you write the mass balance for, in this case, let us say, tungsten? Again the terms remain the same and let us say that again these three terms are dropped; only diffusion is there.

(Professor – student conversation ends)

So what is the corresponding diffusional equation for mass? What would you substitute, instead of  $q$  dot double prime you know, which is heat flux what would you substitute? Mass flux, right? So the mass balance is simply given by divergence of, let us call that  $j$  w dot double prime where  $j$

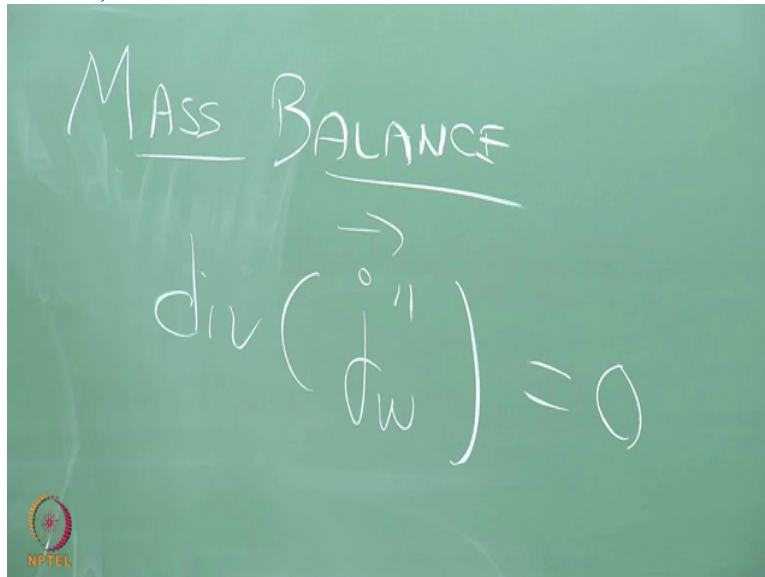
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stands for heat transfer, sorry mass transfer and again the dot is per unit time and the double prime is per unit area.

So basically what we are, this  $j$  w dot double prime is the mass flux

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$$\text{MASS BALANCE}$$
$$\text{div}(\vec{j}_w) = 0$$

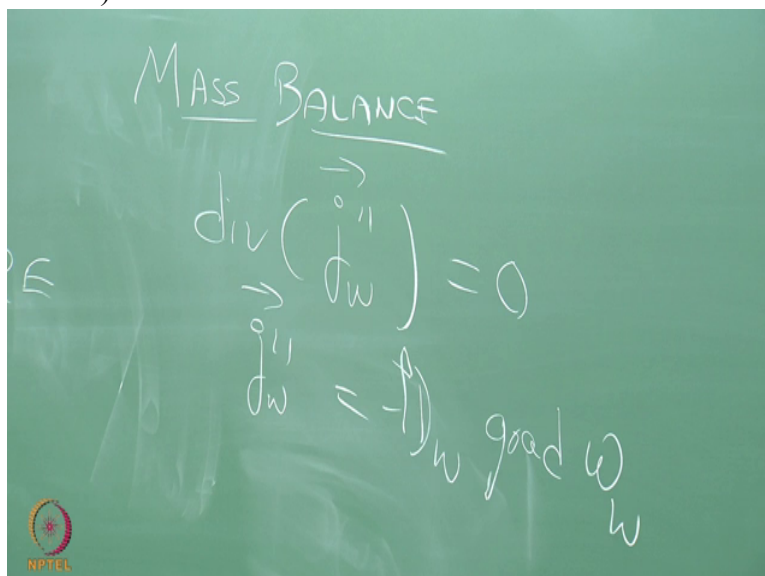
of tungsten expressed in per unit time per unit area. And that must be equal to zero if diffusion is the only process that is inducing transport of the tungsten species. And similarly you will write  $j_w$  as equal to what? What is the mass diffusion flux term?

(Professor – student conversation starts)

Student: Diffusivity

Professor: Minus  $D_w$ , actually that is  $\rho$ , right, density of the gas minus  $\rho D_w$  gradient in  $\omega_w$  where  $\omega_w$  is the

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$$\text{MASS BALANCE}$$
$$\text{div}(\vec{j}_w) = 0$$
$$\vec{j}_w = -\rho D_w \text{grad } \omega_w$$

mass fraction of the tungsten. This is assuming that there is only Fick diffusion happening. Fick diffusion is the diffusion that happens because of the concentration gradient.

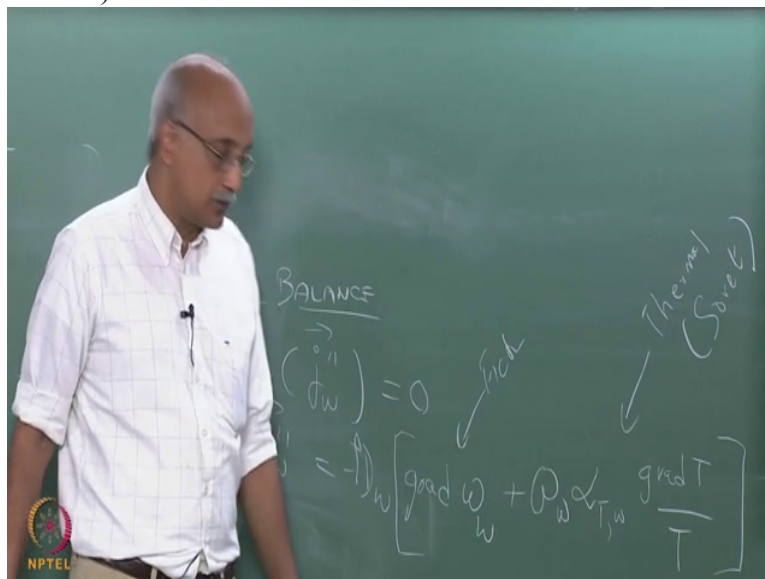
(Professor – student conversation ends)

However there is also something known as thermal diffusion. A diffusion process can also happen because there is thermal gradient. When there is a temperature difference, the molecules are energized to different levels depending on the temperature that they are exposed to. And this difference in energy states can actually drive a diffusional process until equilibration happens.

So when you include thermal diffusion as well, this becomes minus rho D W gradient of omega W plus omega W times alpha T W gradient of temperature divided by temperature. So this is the Fick diffusion part and this is the thermal diffusion part. It is also known as Soret diffusion.

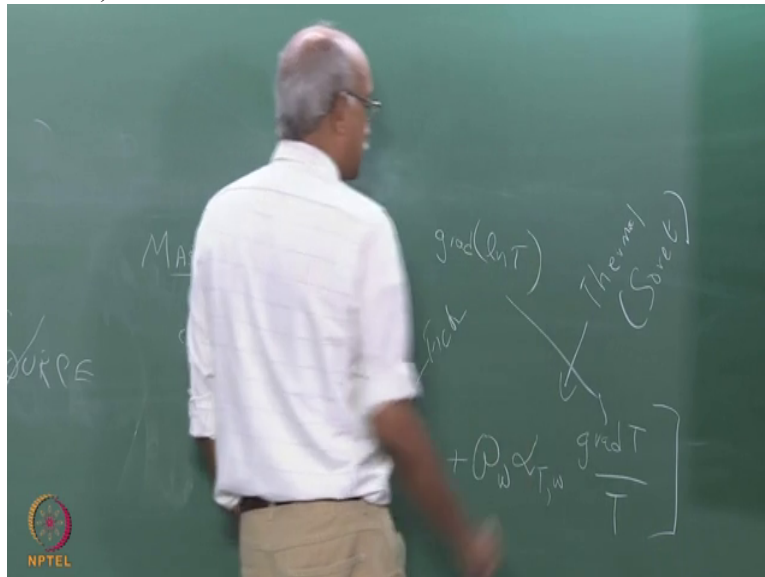
So the complete diffusion equation is minus rho D W which is the Fick diffusivity of tungsten times gradient

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in the mass fraction of tungsten plus omega W, which is the mass fraction of tungsten times the thermal diffusion coefficient of tungsten which is written as alpha subscript T comma W times gradient in temperature divided by temperature which by the way, this term can also be written as gradient in ln of T.

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So essentially you can write for this particular case, the energy balance equation, the mass balance equation, you can apply the appropriate boundary conditions  $T$  at the filament is  $T_f$ ,  $T$  at the wall is  $T_b$ , you have the boundary conditions on the species, you know, you can basically calculate what, what will be the mass fraction of tungsten at the filament, what will be the mass fraction of the bulb and essentially solve the system of equations to get the temperature distribution and from that you can get the concentration diffusion distribution of tungsten.

Once you have the concentration distribution you can calculate the corresponding flux. So you can essentially divide this into various sections and do, you know, finite difference analysis and you know, solve these set of equations and you can calculate a finite rate at which tungsten will evaporate from the bulb and be transported to the, I mean evaporated from the filament and be transported to the bulb wall by a purely diffusional mechanism.

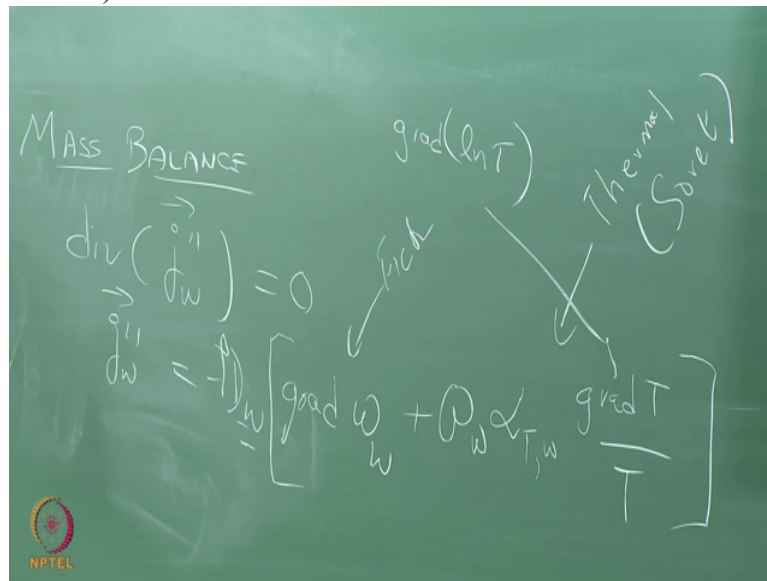
And then you can do a time integration of this and you can actually predict when either the filament will fail because it becomes too thin or the bulb will fail because the layer of the tungsten on the wall becomes too thick. Then you can establish a relationship between light transmission and thickness of the tungsten around the bulb wall and you can determine the failure limit in both cases.

So this is kind of a classical, traditional bulb with a purely P V D process. P V D again implies that the tungsten is present in the gas phase in the same form as it is present in the

condensed phase. And this is case where because it is a purely P V D process there is no way to reverse the process. It will always happen. You can try and slow it down by various methods.

For example if you operate the filament at a lower temperature, that will slow down the rate at which tungsten is evaporating. So that is one way. Or you know you can use heavier gases. You know, this, this D W for example is different

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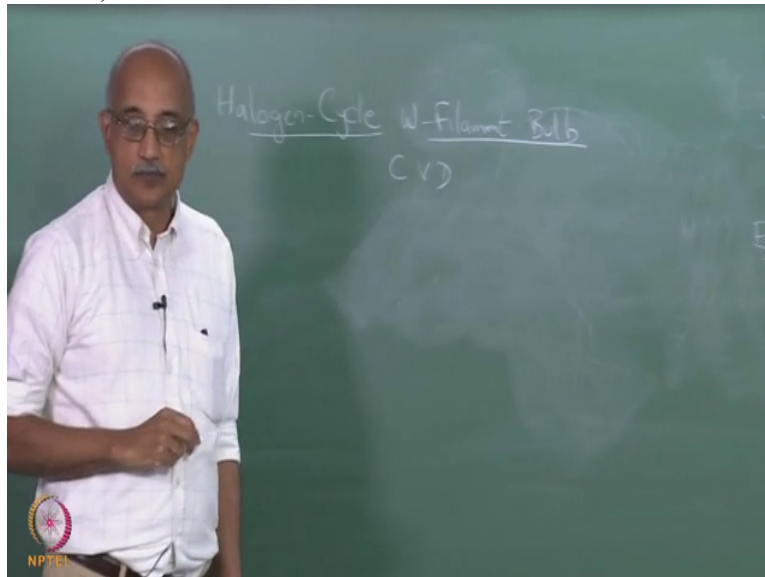


for the various filled gases. The diffusivity of tungsten in vacuum will be very high. But diffusivity of tungsten in a filled environment will be slower.

And by changing the gas that you are using to fill the bulb you can actually control the diffusivity of the species. So if you use heavier gases, larger molecular-sized gases as the filler material the bulb will last longer. Because then the probability that the tungsten molecule will collide with the inert gas molecule and bounce back is greater when the size of the gas molecules is larger.

So you can do some things like that to increase the lifetime of the bulb but eventually it will fail, Ok. So that is why the improvement that was made was to go to a halogen cycle lamp, halogen cycle tungsten filament bulb where now the process that is happening inside is C V D.

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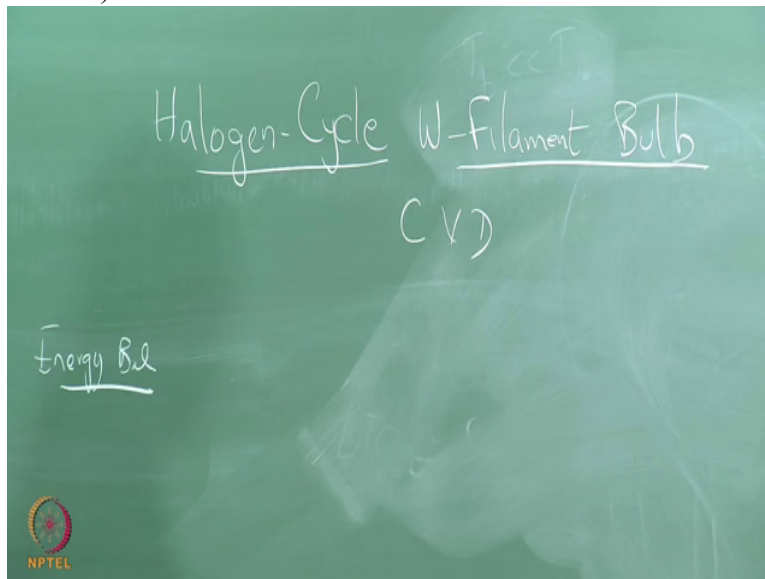


The reason is as soon as you fill it with some reactive gas, the environment becomes chemically reactive. So the tungsten that has evaporated from the filament is not going to stay as tungsten. It is going to be converted to  $WC$ ,  $WC_2$ ,  $WOC_2$ ,  $WO_2C_2$ ; I mean again there are dozens of species that can form. But the material that is going to deposit on the bulb is still tungsten.

So that again is the classic definition of the CVD process where the presence, the identity of the condensed phase is different from the identity of the gas phase species in which it is present. So if you want to take this analysis that we just did and extend it to a CVD process, what, how would it be different?

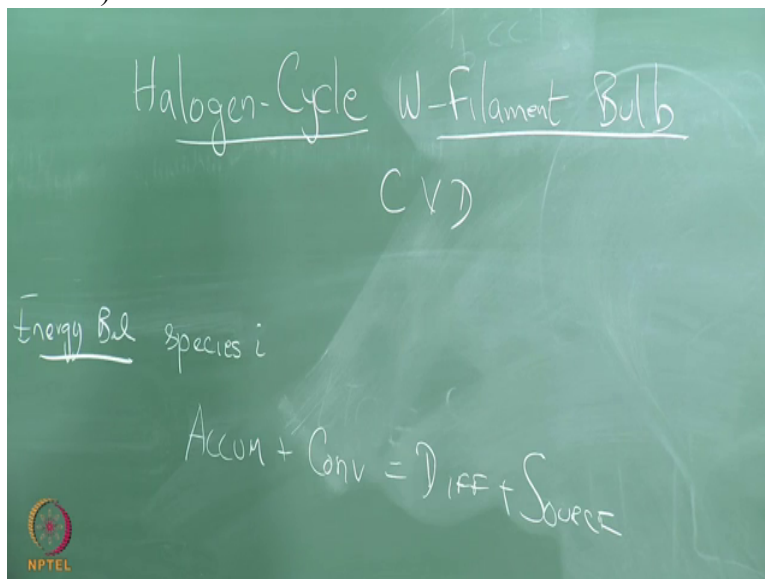
For example if you now do an energy balance,

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can you still drop all the four terms or do you have to keep one of the terms? Suppose you are doing energy balance for species  $i$ . So I still have this equation, accumulation plus convection equals diffusion plus source, so now which of these terms can I drop?

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(Professor – student conversation starts)

Student: Accum/accumulator

Professor: Accumulation

Student: Steady state

Professor: Ok.

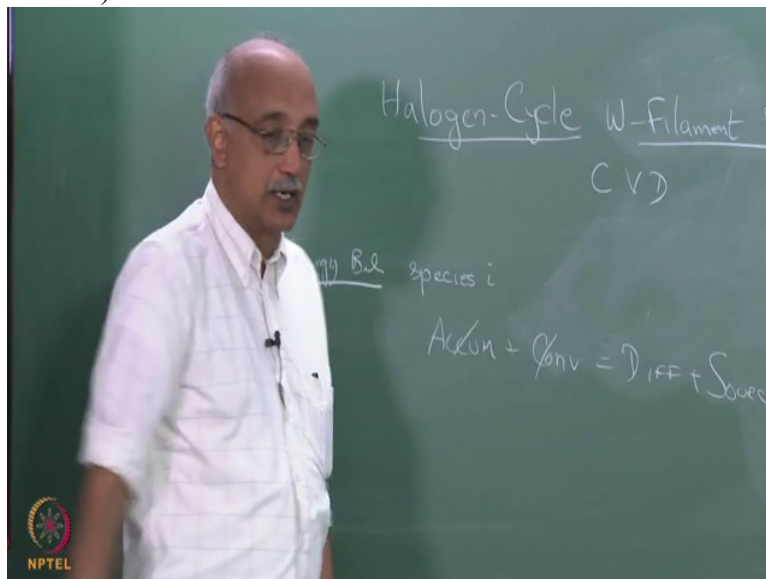


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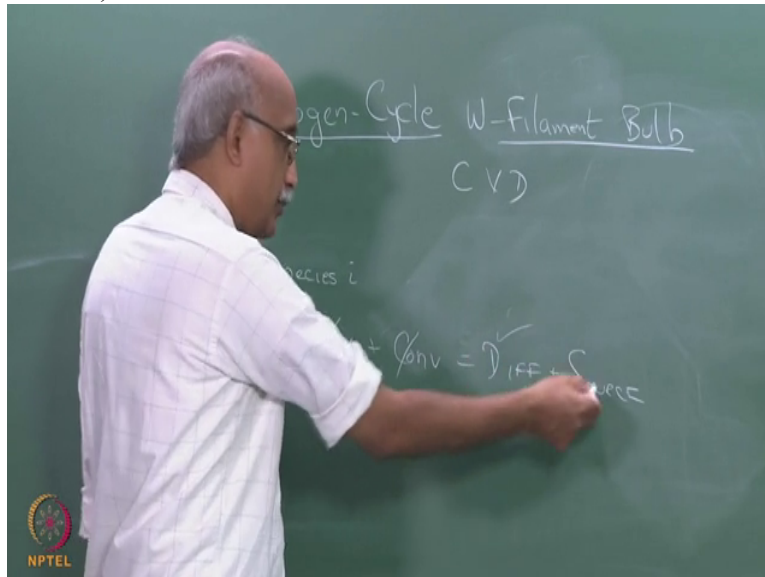
How about convection? We can still drop that because we have not

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done anything to change the fluid mechanic design. The diffusion term should still stay. How about the

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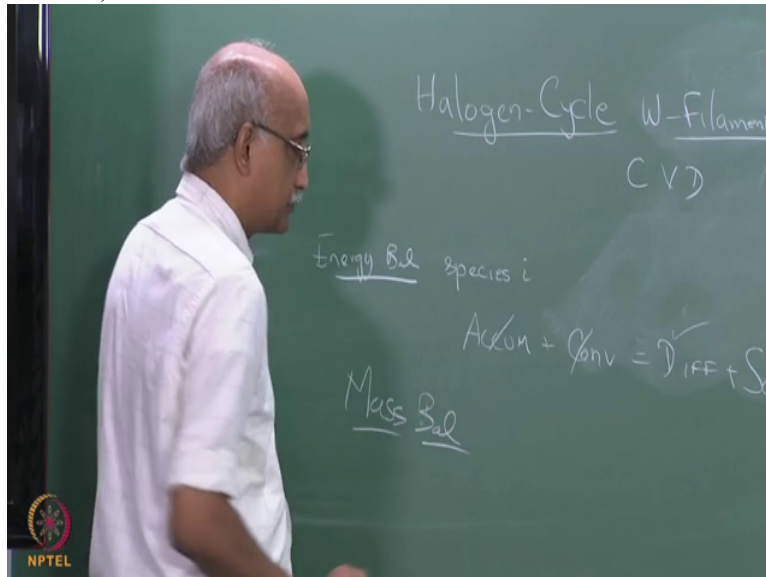
source term? Can you drop it? No it is a chemically reactive environment, right? So for every species there is a source and a sink. Either species are getting generated or they are getting destroyed.

(Professor – student conversation ends)

So now there are two terms in the equation. And so you would have to write your energy balance as a balance between the rate at which energy is getting transported through a diffusional or conduction process balanced by the source term which is that, as chemical reactions happen, they are constantly either generating heat or consuming heat. So the chemical reactions themselves cause changes to the energy conservation term.

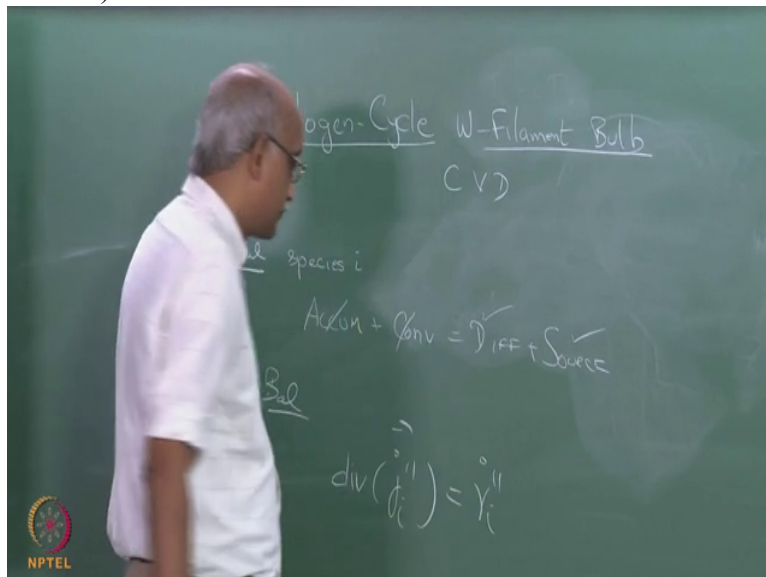
Now if you look at the mass balance term,

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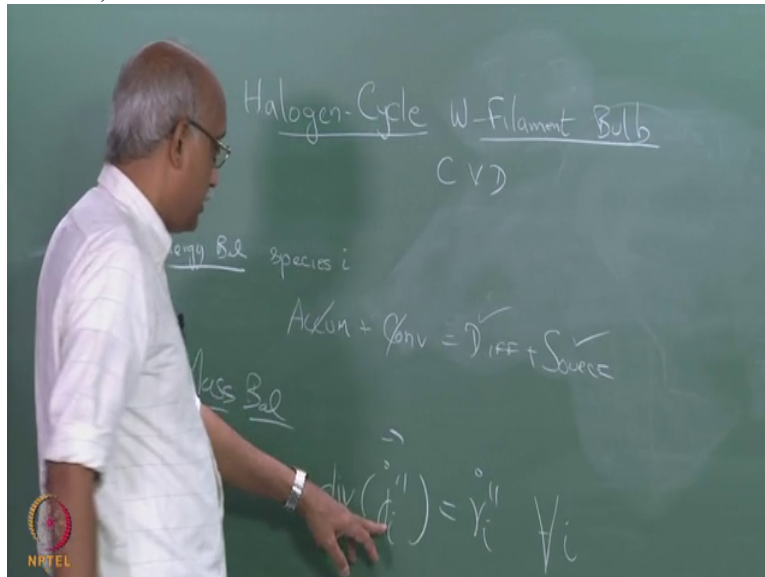
again you now have to keep the diffusional term and the source term intact and write different equations for each species. So for example for the  $i$ th species I would write this as divergence of  $j_i$  dot double prime equals some  $r_i$  dot double prime.

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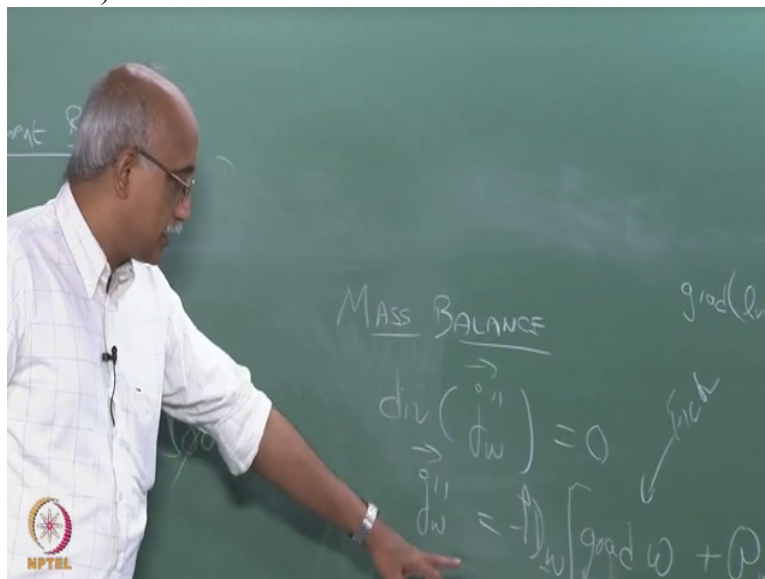
So this is not zero any more. There is a finite rate of reaction associated with each species  $i$ . So the divergence in the flux of the  $i$ th species must be balanced by the rate at which that species is being consumed or produced. And this is true for all  $i$  species and again the diffusional flux of

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$j_i$  double prime will be written in the same format as

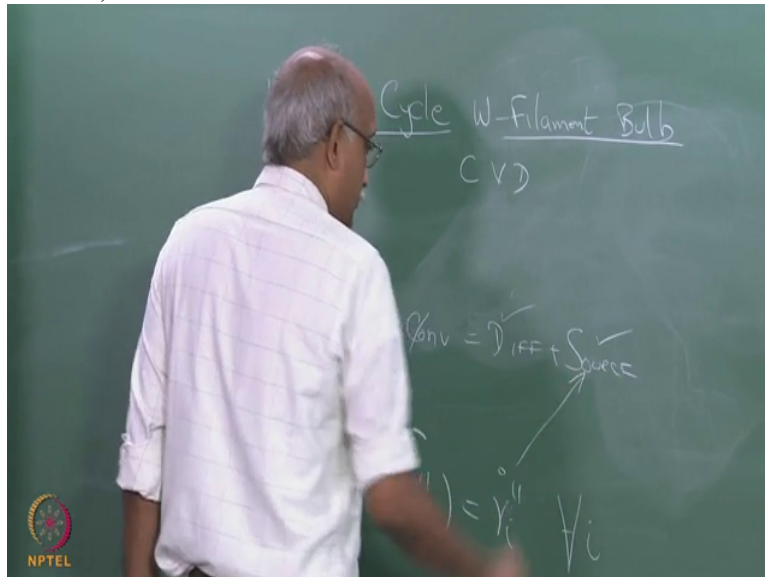
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minus  $\rho D_i$  gradient in  $\omega_i$  plus  $\omega_i \alpha T_i$  grad  $\omega$  I mean grad  $T$  over  $T$  and you have to write this equation for each  $i$ th species and you will now have to also estimate this.

You have to know the reaction rate for every species, the rate at which it is being consumed or produced. If you can do that then you can again, I mean once you know this, from this you can again calculate the

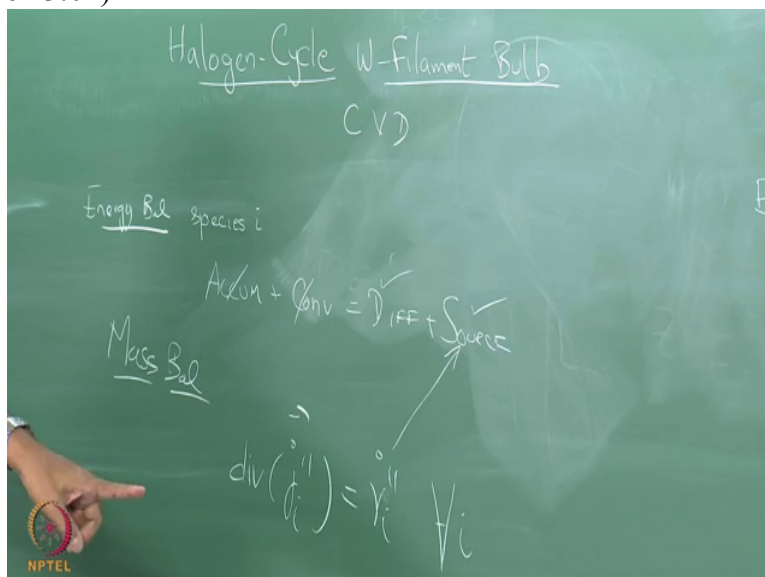
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heat source associated with that based on the enthalpy change and you can again self-consistently solve this.

But as you can imagine, going from there to here is a much more complex process.

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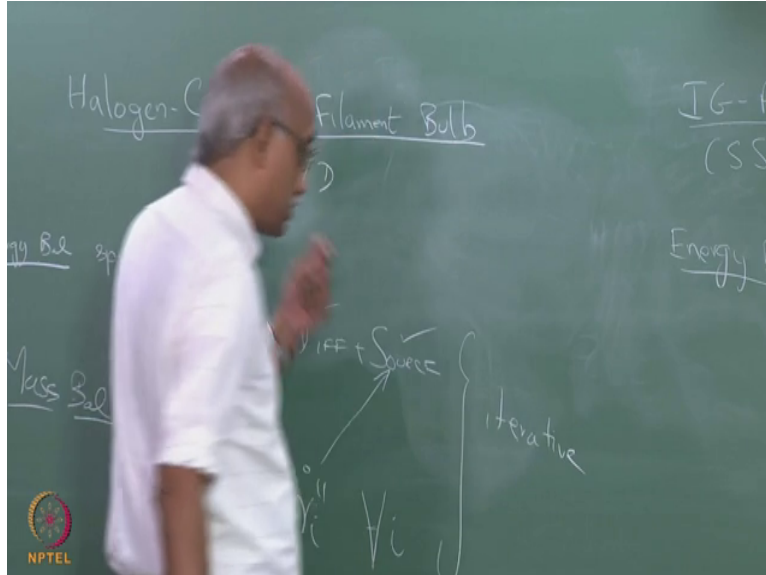
Because now you have to write this balance for every species that is present in the system and it has to be all self-consistent. You know the chemical equilibrium; that the temperature equation and the mass balance equation cannot be decoupled now.

In the previous case, we would have first solved the energy balance equation to set the temperature profiles and then use the diffusion equation to calculate the corresponding diffusion fluxes. In this case you cannot do that because the temperature distribution

influences the chemical reactions but the chemical reactions are also influencing the temperature distribution.

So this has to be solved iteratively in a, as a coupled set of equations.

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Now the only reason you are not including the momentum balance here is because we have made certain assumption that we have a stagnant layer that extends all the way to the bulb, till the walls of the bulb. So this becomes numerically very complex.

I mean there are papers written, there are algorithms that have been produced to do exactly this for various systems of gases filling a bulb. However the numerical complexity involved in solving this error equations in a self-consistent manner is tremendous. So we need a simplified procedure.

How can we take this and simplify it to this? You know how can you apply the same principles that we used for the inert gas-filled tungsten filament lamp and apply that to the analysis, the transport and thermodynamic analysis of a halogen cycle tungsten filament bulb. Is there a trick that we can use that will enable us to do that?

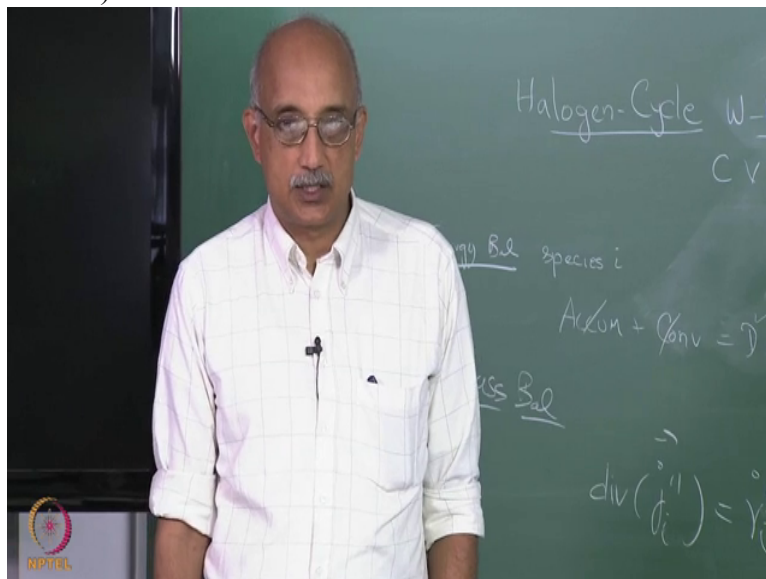
Any thoughts, I mean how would you reduce the complexity of this analysis and make it as simple as that? Why do not you think about it? We will talk about it in the next class

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when we start

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the next lecture, Ok. There is a very simple and elegant way to do this analysis which reduces almost 90 percent of the numerical complexity. Ok, any questions?

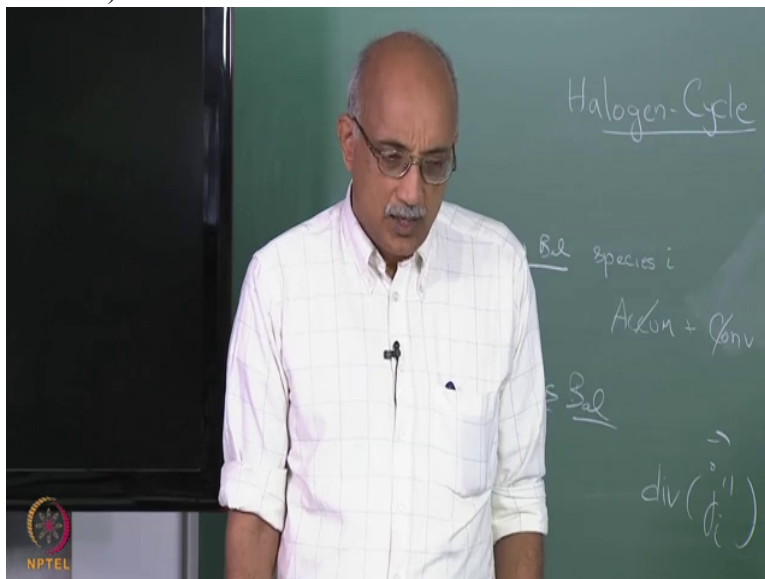
(Professor – student conversation starts)

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Student: Sir the Langmuir layers, how, actually I could not understand that. Langmuir layers, how these are...

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Professor: Langmuir layer by definition is one where transport phenomena are dominated by diffusional processes. For example a boundary layer around an object is a Langmuir layer.

Student: Different, different thickness, different, different density gases are,

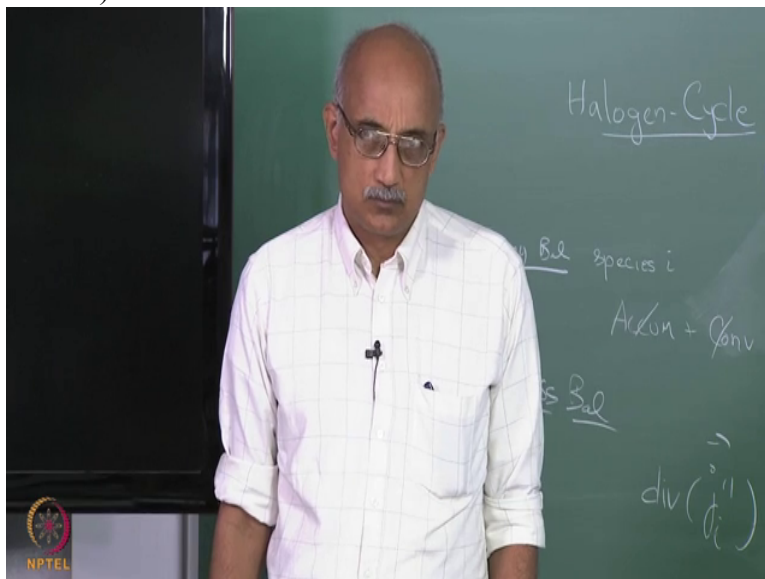


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layer by layer they are depositing on the film?

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Not like that?

Professor: No, this is nothing to do with C V D. A Langmuir layer is a purely fluid mechanical definition. It has nothing to do with our C V D environment. It is a general fluid mechanical definition that in any physical situation where the domain of interest is dominated by purely diffusive phenomena that is known as the Langmuir layer.

(Professor – student conversation ends)

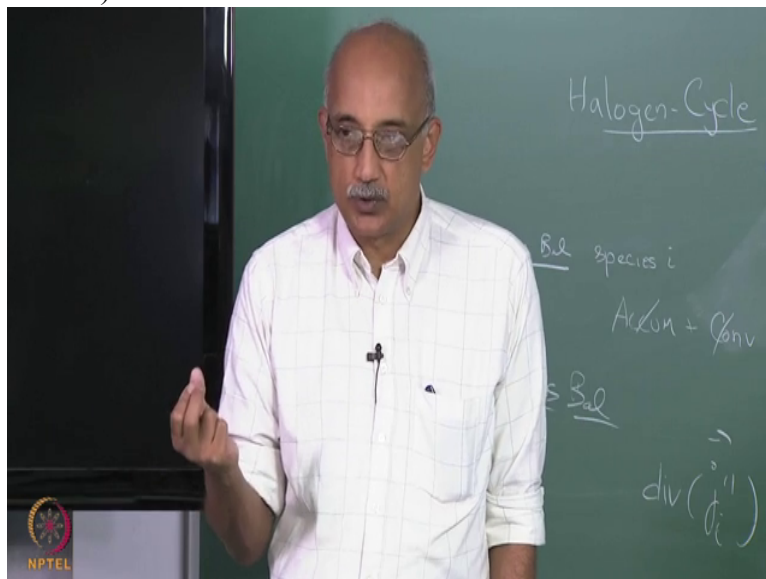
An example of that is a boundary layer. Another example of that is an enclosure like this where you, by design you ensure that only diffusion happens.

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For example flow inside pores, you know micropores, mesopores

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is considered Langmuir flow because it is dominated by diffusive phenomena. So it is a general term that applies to all such classes of flow.

Ok I will see you in the next lecture.