

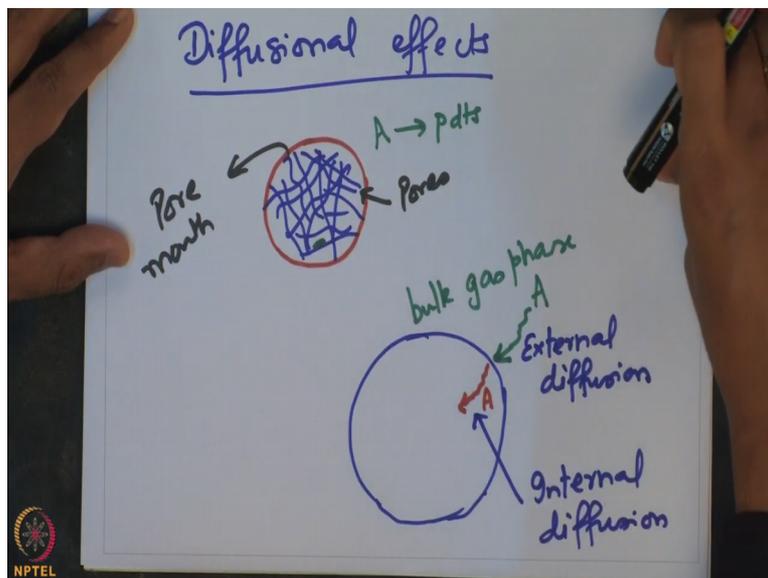
**Chemical Reaction Engineering - II**  
**Prof. Ganesh A Viswanathan**  
**Department of Chemical Engineering**  
**Indian Institute of Technology - Bombay**

**Module - 4**  
**Lecture - 17**  
**Diffusional Effects: Introduction**

Hello. So far, in this course we looked at what is catalysis, what are the different steps in catalysis. We looked at how to find the rate law, what are the rate controlling steps in the catalytic reaction and what is the way to find out the functional form of the rate law from an experimental data. Moreover, we looked at the deactivation of catalyst, what are the different rate laws that may govern the deactivation of catalyst.

Beyond that we looked at how to incorporate these in certain models. Starting today's lecture, we will, in several lectures to come, we will be looking at the diffusional effects which is an important topic in catalysis.

**(Refer Slide Time: 01:21)**



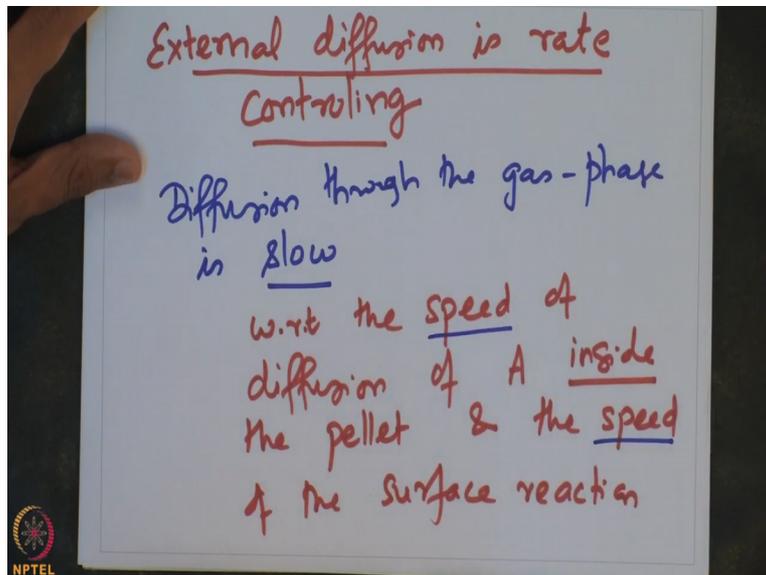
As a recall, if we look at the catalyst pellet structure, suppose we assume a cylindrical catalyst pellet; the catalyst is known to have several pores inside. And each of these pores will have active surface which may be present where the reaction actually happens. So, these are the pores and we can assume that this is the pore mouth. So now, the species A, which is reacting to form products, in order for it to reach the surface where the reaction happens.

The species must actually diffuse from the gas to this exterior surface of the pellet and from there it has to diffuse through the pores to reach the catalyst surface. So, suppose let us say that we depict this process. So, here is the schematic of this process. Species A which is present in the gas, bulk gas phase and undergoes diffusion and reaches the outer surface of the pellet, following which the species has to do an internal diffusion, which happens inside the catalyst pellet till it reaches the surface where the actual reaction happens.

So classically, this diffusion in the bulk phase is what is termed as external diffusion. And the diffusion through the pellet is what is called as the internal diffusion. So, we looked at, in the previous lectures we looked at how to find out the rate law if the steps that is involved in absorption or the surface reaction or the desorption process; if each of these are actually rate controlling.

Now, in several lectures we will now see, what happens if the external diffusion is rate controlling or what happens if the internal diffusion is rate controlling. So, there are 2 possible cases here.

**(Refer Slide Time: 04:24)**



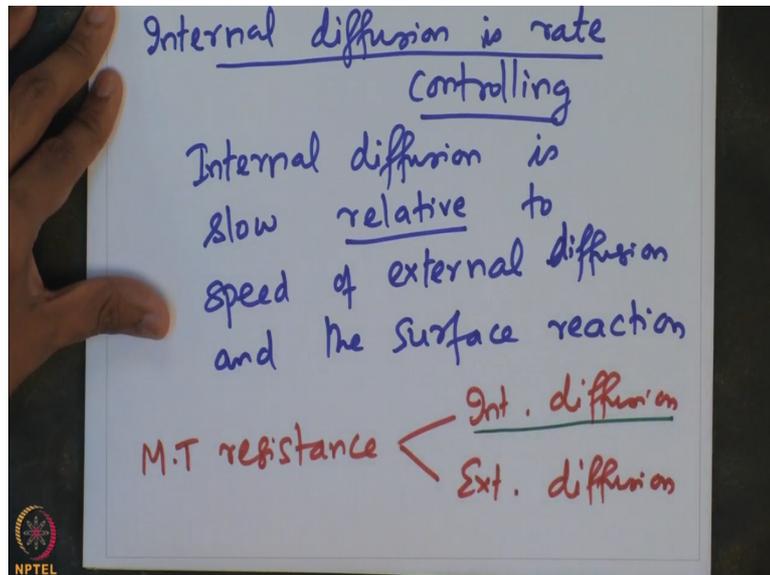
Where external diffusion is rate controlling. In this case, suppose if the diffusion through the gas phase is slow; and note that this process of diffusion of the species through the gas phase is actually an intrinsic property of the species in the medium in which it is present. The diffusivity with which the species molecules actually go from the bulk gas phase to the surface, is actually a property of the species itself. And clearly this diffusivity is going to be different for different species.

So, diffusion through the gas phase for a certain species that is reacting; if that is slow; when I say slow, we must always look at it in terms of a relative terms. So, if it is slow, with respect to the speed of diffusion of species A inside the pellet and the speed of the surface reaction itself. So, if this diffusion is slow compared to the speed of the diffusion of the species inside the pellet and the speed with which the reaction is actually happening.

In that case the overall rate at which the species is being converted to products is actually controlled by the external diffusion process. Now, this is important because the species, if the species diffusion is slow to the catalyst pellet, that as soon as it reaches the surface of the catalyst pellet, the internal diffusion also is fast enough and so the reaction is likely to happen very close to the exterior surface and so most of the catalyst particle pellet inside is actually unused.

So, this actually poses a design challenge, as to how to best utilise the catalyst material and the catalyst that is actually impregnated in the support. So, in future lectures we will actually describe how to quantify the external diffusion process and how to actually identify whether external diffusion is actually rate controlling for a given system. So, the next process that may be rate controlling is the internal diffusion.

**(Refer Slide Time: 07:24)**



So, if internal diffusion, that is diffusion of the species from the catalyst surface to the inside of the catalyst all the way up to the surface, that is via the pores through which the species actually goes inside the catalyst pellet, where the reaction can happen; then the internal diffusion, that speed with which the diffusion happens; if that diffusion is slow, internal

diffusion is slow once again relative to speed of external diffusion and the surface reaction itself.

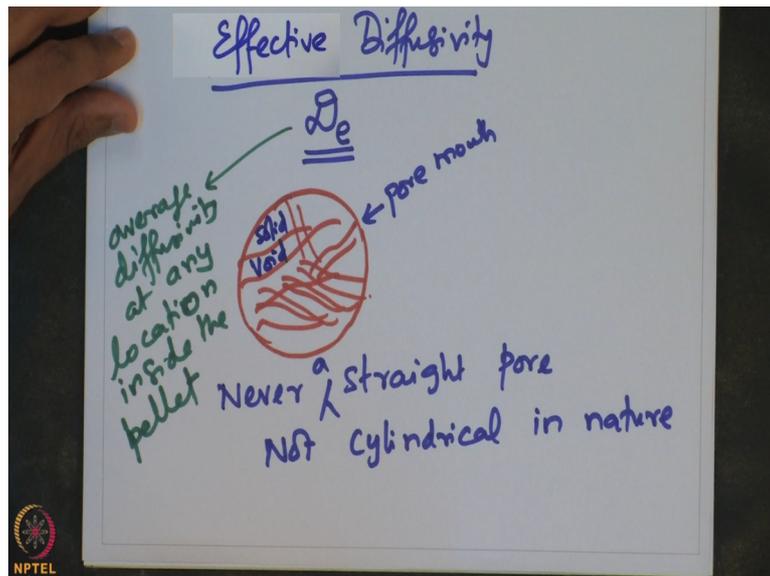
So, in this case, the internal diffusion actually imposes certain resistance for mass transport and therefore the overall rate is essentially controlled by the internal diffusion. So, what it essentially implies is that the external diffusion, the mass transport resistance that is offered, could either be due to internal diffusion or could be due to external diffusion. So, what we will do in the next few lectures is, we will start with characterising if internal diffusion is actually important.

And we will look at how to estimate what is the nature of the resistance that is actually posed due to the slowness of the internal diffusion or because of the de resistance that is offered by the internal diffusion process itself. We will see how to quantify the nature of the resistance and also, we will also find out what are the, we will also describe what are the ways to estimate or identify whether it is the internal diffusion which is actually offering more resistance, that is it is a slower process compared to all other processes, based on the experimental data that may be available.

It is important to note that the observable in this case is essentially the concentration of the species in the gas phase. It is not possible to measure in see, to what is the concentration of each of these species inside the catalyst pores, when the reaction is being conducted or when the reaction is actually happening and the reactor is ran at a certain operating conditions. So, therefore the observable quantity here is the, may be the concentration of the species in the bulk phase.

And so, what are the ways by which to deduce, if the internal diffusion is very slow for a given operating condition and how do you deduce that from the observations that has been made in terms of the concentration of the species in the gas phase. So, we will look at all these in the future lectures.

**(Refer Slide Time: 10:52)**



In order to quantify the internal diffusion process, it is useful to define what is called as effective diffusivity. Typical symbol that is used for effective diffusivity is a  $D$  with a subscript  $e$ . And let us now look at the catalyst pellet again. So, there are several pores which are actually present in the catalyst pellet. And here is the pore mouth, let us say. So, these pores which are present, they are never straight. They are never straight pores through which it is actually, the species is actually diffusing.

And neither they are cylindrical. They are not completely cylindrical. They are not, they are never a straight pore. They are not cylindrical in nature. So, therefore the path through which these species actually flows is actually a tortuous path. So, 1 way to look at this problem is to quantify the diffusion process through each of these pore, where the species is actually going from the mouth of the pore all the way to the inside of the catalyst pellet where the surface reaction is happening.

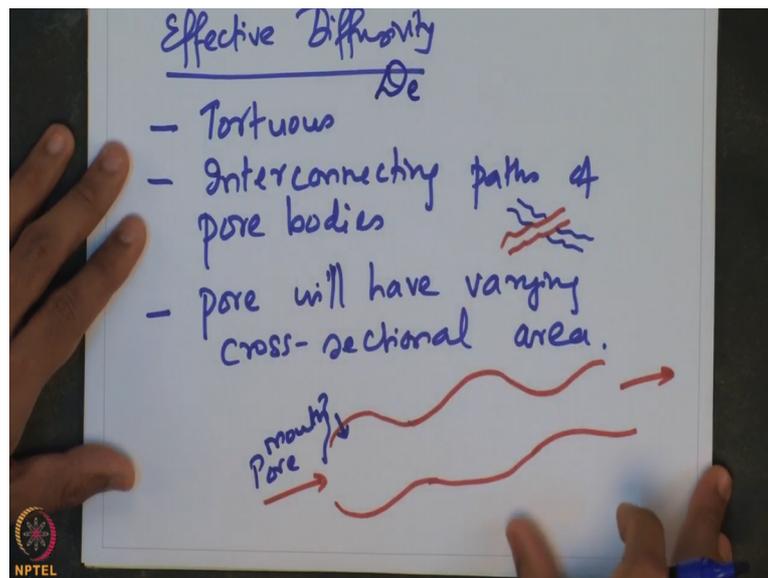
But there are many many pores which are actually present and therefore it is very unfruitful exercise to quantify the internal diffusion process by actually writing model equations for the process that is happening through or the diffusion process happening through each of the pores. So, it is rather convenient to define what is called as an effective diffusivity, which essentially quantifies the average diffusivity at any location inside the pellet.

Now, note that there will be solid play, there will be solid regions inside the pellet. There will be voids inside the pellet. So, the effective diffusivity essentially takes into account all the void solids, everything in, that is present inside and defines an average diffusivity which is

basically valid everywhere inside the catalyst pellet. So, therefore the flux that is actually defined for transport from the surface of the pellet to the inside of the catalyst.

Would now take that into account, where the area through which the species is actually moving via a certain flux, would actually take into account the area that consists of both the voids and the solids. So, the effective diffusivity takes care of the presence of voids and solids. And we will see in a moment, how to define what this average diffusivity is.

**(Refer Slide Time: 14:01)**



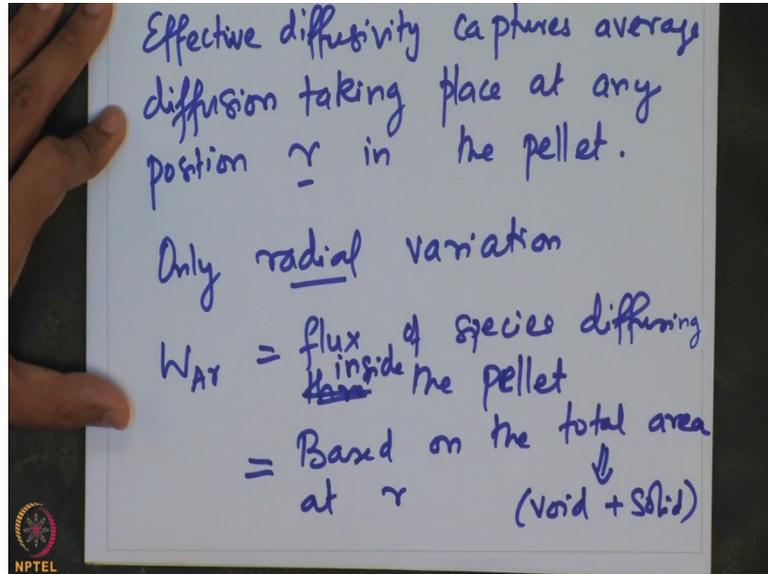
So, effective diffusivity is typically a function of 3 aspects, the pores which are actually tortuous. And it is basically, the pores are interconnecting paths of pore bodies. Lot of these pores, they may be interconnected within itself. So, the effective diffusivity will take into account all of these things. And moreover, the pores will actually have varying cross-sectional area.

For instance, tortuous path, we have already seen in all the sketches, where the pores are actually going through a tortuous path. For, in the case of interconnecting paths, you might have a pore like this and that might be another pore which might actually interconnect with this one. So, there are interconnecting pores which are present. So, clearly, the effective diffusivity should be a function of this.

And the pore will have a varying cross-sectional area. 1 simple way to depict a pore is where the pores actually have a varying cross-sectional area. So, if the species is diffusing, it is experiencing varying cross-sectional area from, let us say the pore mouth. If this is the pore

mouth, all the way to the inside of the catalyst. The species actually experiences varying cross-sectional area. So clearly, the effective diffusivity  $D_e$ , has to take into account all these 3 factors.

(Refer Slide Time: 15:52)



Effective diffusivity essentially captures average diffusion taking place at any position  $r$  in the pellet. So, if we, suppose let us say we consider only radial variation for now; one could in principle consider the azimuthal and the other angle variation in the spherical catalyst pellet. But suppose let us say, we consider only radial variation for now. So, the flux  $w_a r$ ; if  $w_a r$  is the flux of species diffusing through the, inside the pellet; then this should be based on the total area, at any radial position or which basically includes the voids + the solids that may be present.

That is because the presence of voids and solids is already taken into account in the effective diffusivity. And therefore, the flux that we defined for a species that is diffusing through the pellet must be based on the total surface area that is available, which includes both the voids and the solids.

(Refer Slide Time: 17:45)

$$D_e = \frac{D_{AB} \phi_p \sigma_c}{\bar{\tau}}$$

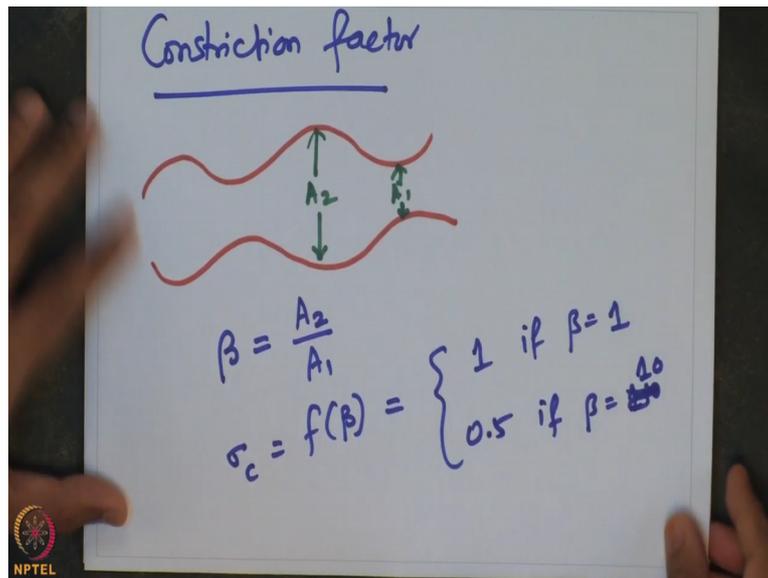
$\phi_p = \text{pellet porosity} = \frac{\text{Vol. of void space}}{\text{Total volume}}$   
 $\sigma_c = \text{constriction factor}$   
 (variation in cross-sectional area)  
 $\bar{\tau} = \text{tortuosity} = \frac{\text{Actual distance a mol. travels bet. two pts}}{\text{Shortest dist. bet. them}}$

So, the effective diffusivity  $D_e$ , can essentially be written as, the equimolecular counter diffusivity of the species, through the, for the species, reacted species and the product species that is being considered; that multiplied by  $\phi_p$  which is essentially the pellet porosity and  $\sigma_c$  is essentially constriction factor, which, and then the  $\bar{\tau}$  is actually the tortuosity. So,  $\phi_p$  is the pellet porosity, which is = the volume of void space, divided by the total volume.

And  $\sigma_c$  is the constriction factor, which takes into account the variation in cross-sectional area. And  $\bar{\tau}$  is the tortuosity which is defined as the actual distance a molecule travels between 2 points, divided by the shortest distance between them. We will see in a moment, how to actually find out what is constriction factor. So, the effective diffusivity is essentially a function of the pellet porosity which takes into account the voids and the solid fraction of voids and the solids.

And then it is a function of the tortuosities which takes care of the tortuous path that the pores actually have. And therefore, the species diffuses through this tortuous path. And also the  $\sigma_c$  which is the constriction factor, which takes care of the variation in the cross section area in the pores through which the species actually diffuses from the surface of the pellet to the place, to the location where the reaction actually happens.

**(Refer Slide Time: 20:09)**

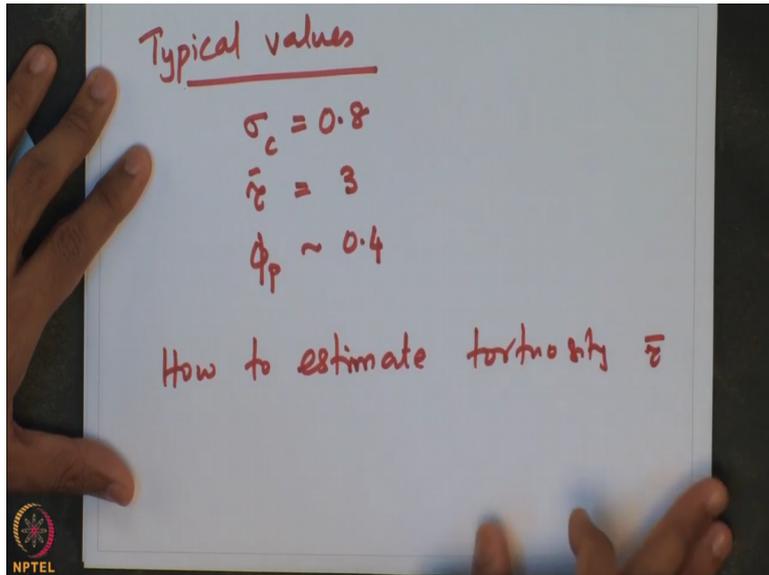


So, let us look at how to find out what is sigma c, which is the constriction factor. Suppose we have a pore with varying cross-sectional area. And if I now define this area as, let us say  $A_2$ . And this area, let us say is  $A_1$ . And I define a quantity called beta, which is essentially the ratio of  $A_2$  divided by  $A_1$ ; which is essentially the ratio of the area which is at the largest location divided by that of the smallest location.

And so, the smallest gap that is present or smallest cross section area and  $A_2$  is like the large cross section area. So, sigma c is essentially a function of this quantity or this ratio of cross-sectional areas. And typically, if beta is = 1, then the sigma c is = 1 if beta is = 1. And if beta is = approximately 10, then the sigma c value is approximately 0.5. So, there is a functional dependence and that would depend on the nature of the pellet and the shape and the geometry of the pellet that is being considered.

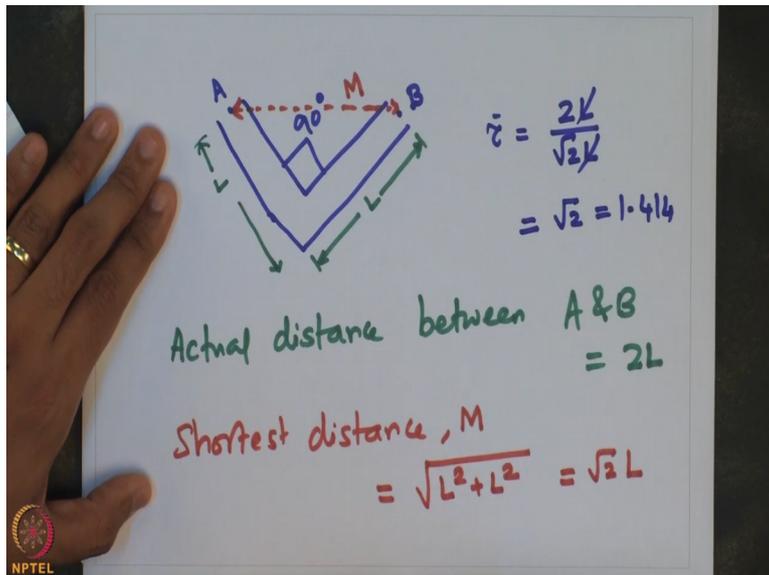
So, it is 1 if beta is = 1 and it is 0.5 typically if beta is = 10. So now, if suppose, so suppose we want to know what are the typical values for these constants.

**(Refer Slide Time: 21:49)**



So, the typical numbers, typical values are sigma c which is the constriction factor; it is about 0.8. And tau bar which is the tortuosity; it is about 3. And the porosity typically is about 0.4. So, let us look at how to estimate tortuosity. Let us take an example. Suppose we have a right angle bend in one of the pores.

(Refer Slide Time: 22:29)



Suppose we consider a right angle bend and let us say that the species is moving from point A to point B. And if the length of 1 side, let us say is L and let us say that the length of the other side is also the same length as that of the first arm of this tortuous path. So now, what is the actual distance that is traveled between? What is actual distance between A and B that a species would travel?

So, the actual distance between A and B, that is  $= 2L$ . And what is the shortest distance? The shortest distance is essentially this distance indicated by this dashed line. So, the shortest distance, let us say the shortest distance is, let us say  $M$ . So, this shortest distance  $M$  is essentially given by square root of  $L^2 + L^2$ , which is essentially  $= \sqrt{2}$  times  $L$ .

So, from here we can easily deduce that for this example the tortuosity  $\tau$  is essentially given by the actual distance to  $L$ , divided by the shortest distance's square root of  $2$  into  $L$ . And that is  $=$ , if you cancel out these, that is  $=$  essentially square root of  $2$  which is  $1.414$ . So the, so this is the way to estimate tortuosity for a given pore actually that is present. And one can actually find out for different pores and one can, for different geometries, one can actually estimate the tortuosity that may be present.

And that may help in finding out what is the average tortuosity for a given catalyst pellet. So, what we have seen in this lecture is what are the different diffusive processes which may be rate controlling. That is the internal diffusion or the external diffusion. And we started looking at quantifying the internal diffusion. That is diffusion of species inside the catalyst pellet from the outer surface of the catalyst to the location where the reaction might happen.

And this is very important from design point of view. So, what we looked at is the first step in terms of quantification, where we defined the effective diffusivity which essentially captures the average diffusivity at any location or assuming that the overall area that is available, is available for the flux of the species or diffusion of that particular species. So, from next lecture will start looking at actually writing the balances for the internal diffusion process and will quantify the internal diffusion process, starting from the next lecture. Thank you.