

Chemical Reaction Engineering - II
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Module - 7
Lecture - 31
Overall Effectiveness Factor I

In the last lecture we completed the case of external mass transfer limitations. That is the resistance offered due to diffusion of species from bulk to the surface of the catalyst pellet. Now, the question arises as to what happens if all these different resistances actually are comparable. In the first topic on the diffusional limitations we observe that, when there is internal diffusional limitations and there is no external mass transport limitations then we could use, define a quantity called the effectiveness factor or internal effectiveness factor.

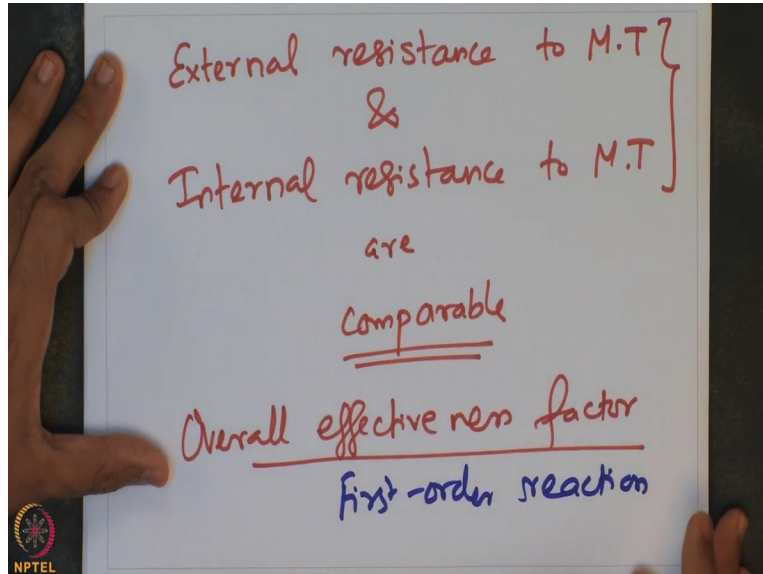
And if the surface reaction is actually controlling, then it is intrinsic kinetics which actually controls the overall rate of the reaction. Now, if it is the, simply the internal diffusion which is controlling and the external mass transport resistances are negligible, then it is just that the effectiveness factor multiplied by the rate at which the reaction is happening at the surface conditions, that essentially gives the overall rate at which the reaction happens.

Now, it is usually not the case that the reaction happens either at the external mass transport resistance regime or the internal diffusional limitation regime or completely the reaction controlling regime. Often the typical operation would be somewhere in-between, where the resistances to the external mass transport could be comparable to the resistances to the internal mass transport. And therefore, one has to actually consider all of these aspects together.

Now, often it turns out that it may be desirable to operate under that particular type of situation where the external resistance to mass transport and the internal resistance to mass transport are actually comparable. It might be desirable to have a design of a reactor and operating condition where the operation actually might be under these 2 conditions for a certain system could actually give better productivity than purely internal diffusional resistances or purely resistance to mass transport.

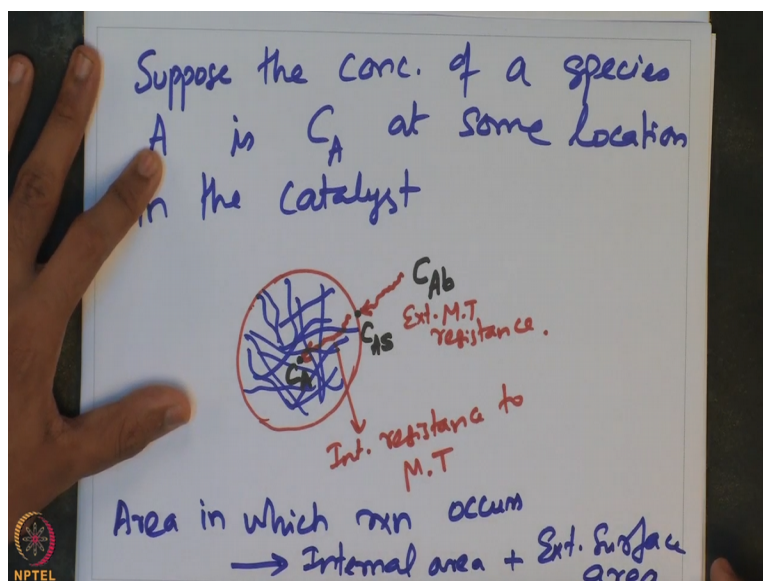
So, the question arises as to how do we quantify if both these resistances are comparable and are simultaneously present. Which is what we going to see in the next couple of lectures starting now.

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We will assume that external resistance to mass transport and internal resistance to mass transport are actually comparable. So, we are going to look at what is called as the overall effectiveness factor. We are going to define a quantity called overall effectiveness factor in this lecture, which essentially would account for the external resistance to mass transport and the internal resistance to mass transport. And we will particularly look at the case of a first order reaction. We will look at the case of a first order reaction.

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Suppose, the concentration of a species, let us say reacting species A, is let us say C_A at some location in the catalyst. So, let us now sketch a catalyst here. Suppose, we have a catalyst, spherical catalyst, let us say. And the pores that are present here; these are let us say the pores in the catalyst pellet. And let us say that these bulk concentration of the species, let us say is $C_{A \text{ bulk}}$. And the surface concentration of the species let us say is $C_{A S}$.

And the concentration of the species at some location inside the catalyst is C_A . So, now we have species which is actually diffusing from bulk to the surface of the catalyst. And then there is resistance that is offered because of this diffusion and that is the external mass transport resistances. And then, there is a resistance that is offered for transport inside the catalyst. That is, species going from surface, which is at surface concentration $C_{A S}$ to some concentration C_A inside the catalyst.

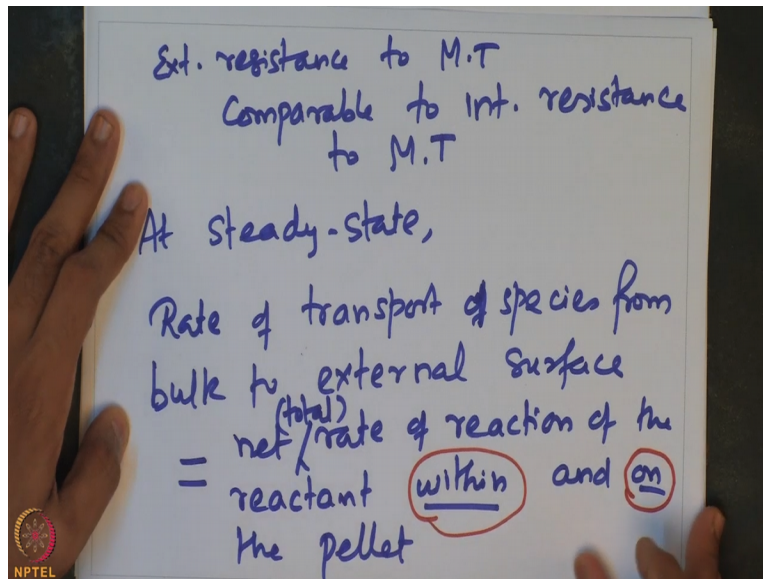
So, this is essentially the internal resistance to mass transport. Now, earlier we observe that, when the external mass transport resistance is the only resistance which is significant compared to the internal mass transport resistances, then essentially the reaction would get completed very close to the external surface of the catalyst. On the other hand, if external mass transport resistances are very small compared to the internal resistance, then the reaction would actually happen in several parts inside the catalyst in the active surface area in the pores.

And the level, extent to which the species penetration happens inside depends upon the extent of the internal resistance that is offered to the mass transport. So, as a result, one can actually think of a situation where the, if the resistances are comparable for both the external resistance for mass transport and the internal resistance for mass transport, then it turns out that the reaction would happen both at the surface or close to the surface of the pellet.

And also in the active surface in the pores inside the catalyst pellet. So, what is the reaction area? What is the area in which the reaction happens now? If this is comparable, the area in which reaction occurs would be internal area + the external surface area. So, the reaction would essentially happen on both the internal and external surface area. So, if we now say that these 2 resistances are actually comparable, then we will have to consider the area where the reaction happens as both the external surface area of the catalyst pellet across the whole reactor bed.

And also the internal catalyst pellet, internal area which is available in every catalyst which is present in the bed. So, let us see how to considered both of these simultaneously.

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So, suppose let us say that the external resistance to mass transport is comparable to internal resistance to mass transport. Then at steady-state, what will be the rate at which the overall reaction will occur? So now, the rate at which the overall reaction would occur in the catalyst would be = the rate at which the species actually diffuses from the bulk to the surface of the catalyst pellet. Why is that?

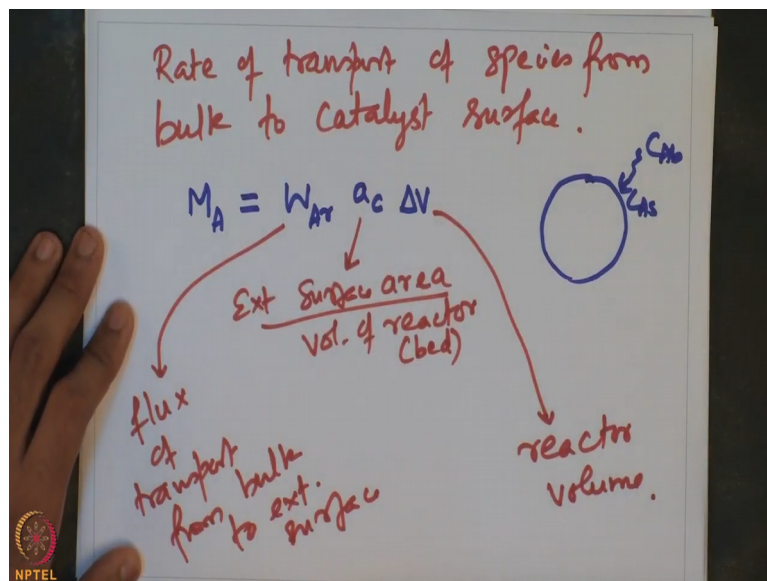
Let us look at the sketch we draw a little while ago. So, the rate at which the species comes to the surface will be comparable to the rate at which at steady-state should be = the rate at which the species actually goes inside the catalyst, because they are actually, the resistances are comparable. And therefore, the overall rate at which the reaction occurs should essentially be = the rate at which the species is transported from bulk to the surface.

Because this is, this rate is what makes the species available for the reaction to happen. And therefore, the rate at which the species is transferred from the bulk to the surface should be = the rate at which the reaction actually happens or the overall rate at which the reaction happens in the catalyst pellet. So therefore, the rate of transport of species from bulk to external surface, that should be = the net rate or total rate of reaction of the reactant within and on the pellet.

Recall the, recall the point that I mentioned a few moments ago that when both the resistances are comparable, then the reaction essentially happens both at the surface of the catalyst pellet and also in the active surfaces inside the catalyst pellet where the reactants are available. So, therefore the net rate of the reaction is essentially within and on the catalyst pellet.

And therefore, we, if we have to equate the rate of transport of the species from bulk to the external surface to the total rate of reaction, then we should consider both the surface area available for reaction within the pellet and also on the external surface of the catalyst pellet.

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So now, if I want to find out what is the rate at which, rate of transport of species from bulk to catalyst surface. How do I do this? We have already seen this before. The rate at which the species gets transported from the bulk to the surface can be related to the flux of the transport of the species from the bulk to the catalyst surface. Let us see how to do that.

So, the molar rate at which the species is transferred from the catalyst bulk, so the bulk to the surface of the catalyst pellet, that should be = whatever is the radial flux with which the species is transported from bulk to the catalyst surface, that multiplied by the surface area per unit volume of the reactor multiplied by the volume of the reactor. Note that, we now want to consider that the bed is actually the catalyst particles are present in the, all thorough the bed.

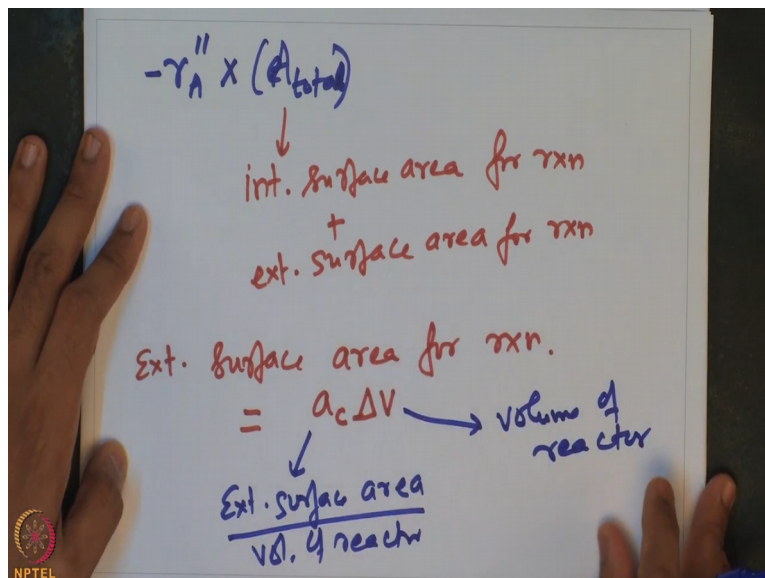
And the reaction is actually happening at the every catalyst pellet, the surface of the catalyst pellet and inside the catalyst pellet, all through everywhere in the reactor. So therefore, we

need to now consider the reactor volume as well. And that is what ΔV here represents essentially the volume of the reactor. What is a_c ? a_c is the, a_c is the surface area, external surface area per volume of the reactor or volume of the bed.

And this is the flux of transport from bulk to external surface. And this is the reactor volume. Now, why do we consider external surface area here? We consider external surface area because the species which is actually diffusing from the bulk to the surface essentially is dictated, the flux is essentially happening at the external surface area. So, therefore we need to look at what is the total external surface area which is available per unit volume of the reactor bed.

And that is what is essentially captured by this quantity a_c here. Now, this needs to be equated to the rate at which the reaction is actually happening within and on the external surface of the catalyst pellet. Let us see how to do that.

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So, $-r_A''$ which is the rate at which the reaction happens per surface, per unit surface area available for the reaction. And that is essentially, has to be multiplied by the total area, A_{total} which is available for the reaction. Now, how do we find the total area which is available for the reaction? We just observed that A_{total} is basically the internal surface area which is available + the external surface area which is available.

For the reaction to occur, internal and the external surface area. So, that is the total area which is actually available for the reaction to happen. Now, let us first estimate what this total

area is. How do we calculate the external surface area? Let us start with the external surface area. So, external surface area for reaction is essentially given by a c which is the external surface area per unit volume of the reactor multiplied by the volume of the reactor itself.

So, this is the external surface area per volume of the reactor. And this is the volume of the reactor itself. How do we find the internal surface area? Let us look at how to find the internal surface area.

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The image shows a whiteboard with the following handwritten text:

Internal surface area

$$A_{int} = \frac{\text{Internal area}}{\text{Mass of catalyst}} \times \frac{\text{Mass of catalyst}}{\text{Vol. of catalyst}}$$

$$\times \frac{\text{Vol. of catalyst}}{\text{Vol. of reactor}} \times \text{Vol. of reactor}$$

$$= S_a \rho_c (1 - \phi) \Delta V$$

An arrow points from the term $(1 - \phi)$ in the final equation to the word "porosity" written below it.

So, the internal surface area is essentially given by, internal surface area for reaction is essentially given by, is the internal area per mass of the catalyst. Typically, the information about a catalyst pellet, the area available, internal area which is available; recall that the catalyst is actually let us say porous catalyst and there are pores which are present. And each of these pores will now have active surface which is coated with the corresponding active catalyst material.

And therefore, characterisation of a catalyst pellet would actually give you the information of what is the total area which is available, what is the total surface area which is available in the pores for the reaction to happen per unit weight of the catalyst. That is an important specification property for a catalyst pellet. And so, we can capitalise on that information to find out what is the total internal area which is available for reaction in a bed.

Let us see how to do that. So, this internal area per mass of catalyst is typically available as a property of the catalyst. And that multiplied by mass of the catalyst per volume of catalyst,

which is nothing but the density of the catalyst. And that multiplied by volume of catalyst per volume of the reactor. And that multiplied by volume of reactor will essentially give you what is the total internal area which is available.

Note that this term here is nothing but the density of the catalyst. And this term is actually related to the porosity of the bed, porosity with which the reactor is actually packed with the catalyst. That tells us what is the ratio of the volume of the catalyst versus the volume of the reactor. So, let us plug all these information in. So, suppose S_a is the internal area per mass of the catalyst and ρ_c is the density of the catalyst that is available.

That information is available too. Multiplied by volume of the catalyst is essentially divided by the reactor, is essentially $1 - \phi$, where ϕ is the porosity of the, ϕ is essentially the porosity. And that multiplied by ΔV will tell me what is the internal area which is actually available for the reaction to happen inside the pores. Now, once we know what the internal and the external area is available we can actually find out what is the overall rate at which the reaction happens in the catalyst pellet. Let us see how to do that.

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$$\begin{aligned}
 A_{total} &= A_{ext} + A_{int} \\
 &= a_c \Delta V + S_a \rho_c (1-\phi) \Delta V \\
 &= [a_c + S_a \rho_c (1-\phi)] \Delta V
 \end{aligned}$$

$\rho_c (1-\phi) = \rho_b$ Bulk density.

$$A_{total} = [a_c + S_a \rho_b] \Delta V \Rightarrow \text{Total area available for reaction}$$

So, A_{total} is = the external area which is available for reaction + the internal area which is available for the reaction. What is the external area which is available? We already saw that. That is the area which is available per unit volume of the reactor multiplied by ΔV which is the volume of the reactor. And the internal area we just looked at is the area of the active surface per mass of the catalyst multiplied by the density of the catalyst into what is the volume of the catalyst per volume of the reactor into ΔV .

And that is nothing but $a_c + S_a \rho_c$ into $1 - \phi$ multiplied by ΔV . What is ρ_c into $1 - \phi$? ρ_c is the density of the catalyst and that multiplied by the volume of the catalyst divided by the volume of the reactor essentially tells me what is the bulk density of the reactor. So, the mass of the catalyst per volume of the catalyst multiplied by the volume of the catalyst that is packed in a reactor divided by the volume of the reactor.

It is nothing but the bulk density of the catalyst in the reactor. So therefore, if I say this is my bulk density, I can rewrite the total area available as $a_c + S_a$ into ρ_b into ΔV . So, this is the total area available for reaction all through the bed. That is, in the total volume of the bed, what is the total area which is available for the reaction to happen is essentially given by this expression here.

So, once we know this expression, we can actually substitute that into the overall rate at which the reaction happens in terms of the surface area which is available for the reaction. That, if we multiply, we will be able to find out what is the overall rate at which the reaction happens at steady-state. Let us look at that.

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Total rate at which the reaction occurs :-

$$-r_A'' A_{\text{total}}$$

$$= -r_A'' [a_c + S_a \rho_b] \Delta V$$

= Rate of transport of species from bulk to the catalyst surface

So, total rate at which the reaction occurs is essentially given by $-r_A''$, which is the rate per unit surface area, that multiplied by the total area. And that is $-r_A''$ into $a_c + S_a$ into bulk density into ΔV . So, this is the overall rate at which the reaction happens. Now, we observed that this rate should be = the rate of transport of species

from bulk to the catalyst surface. Now, we already saw what is the expression for this particular rate of transport. And that is =;

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$$M_A = W_{AY} a_c \Delta V$$

$$= -r_A'' [a_c + S_a \rho_b] \Delta V$$

Silical-Alumina Spherical Catalyst Pellet

pellet diameter $\Rightarrow 3 \text{ mm} = \underline{\underline{3 \times 10^{-3} \text{ m}}}$

Bed porosity = $\underline{\underline{0.3}}$

So, the rate of transport and M_A is = the flux with which the species is transported from bulk to the surface multiplied by the area per unit volume of the bed multiplied by the volume of the reactor itself. So now, equating this to the overall rate at which reaction happens; that should be = $-r_A'' [a_c + S_a \rho_b] \Delta V$. So, this is the balance between the transport of species from bulk to the surface and the rate at which the reaction happens in the catalyst.

Now, we know what is the expression for the flux with which the species is transported. And we can now substitute that and we can find out what is the relationship between the transport of species from the bulk to the surface to the overall rate at which the reaction happens. But before we do that, let us look at the quantitative range for these 2 values. Let us take a specific example.

Suppose, we take the silica alumina spherical catalyst, let us take the silica alumina spherical catalyst pellet. What is the typical size of a catalyst pellet. We already saw several examples in this course. We even saw the actual catalyst, how it looks like. So, typically, the diameter of a catalyst pellet which is typically about 3 millimetres, which is = the pellet diameter. Pellet diameter is approximately 3 millimetres which is = 3×10^{-3} metres.

Now, what is the typical bed porosity? Suppose we assume that the bed porosity is about 0.3. Suppose we assume that the bed porosity = 0.3, we can estimate what is the surface area which is available for the reaction per reactor volume. And we can also estimate what is the surface area which is available inside the pellet and multiplied by the density to get a quantitative comparison of the values for these 2 quantities. Let us see how to do that?

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The image shows a whiteboard with the following handwritten content:

$$a_c = \frac{6(1-\phi)}{d_p} = \frac{6(1-0.3)}{3 \times 10^{-3}}$$

Below the first equation, a red arrow points from the term d_p to the text "diameter of catalyst pellet".

$$= \frac{6 \times 0.7}{3 \times 10^{-3}}$$

$$\approx 1400 \frac{\text{m}^2}{\text{m}^3}$$

Below the final result, a red arrow points down to the text "Surface Ext. Area per reactor volume available for the reaction".

So, the surface area per unit volume of the reactor for a spherical particle is essentially given by $6(1-\phi)/d_p$. d_p is the particle diameter, diameter of the catalyst pellet. And so, we substitute these numbers. It will be $6(1-0.3)/3 \times 10^{-3}$. So, that is $= 6(0.7)/3 \times 10^{-3}$, which is essentially \approx , approximately $= 1400$ metre square per metre cube. So, this is the area, external surface area per reactor volume available for the reaction.

So, that is the typical external surface area per unit volume of the reactor that is available for the reaction. Next, let us look at the, let us look at what is the internal surface area which is available.

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Internal Surface area

$$\sim 300 \text{ m}^2/\text{g of catalyst}$$

$$\rho_b = \rho_c (1 - \phi)$$

Silica Alumina Catalyst

$$= 400 \times 10^3 \times (1 - 0.3)$$

$$= 280 \times 10^3 \frac{\text{g}}{\text{m}^3}$$

$$\rho_c = 400 \frac{\text{kg}}{\text{m}^3}$$

$$S_a \rho_b = 300 \times 280 \times 10^3 = \sim 84 \times 10^6 \frac{\text{m}^2}{\text{m}^3}$$

So, let us now calculate what is the typical internal surface area which may be available. So, the typical internal surface area for these kinds of catalysts. We have looked at some of these numbers. It is typically of the order of magnitude of 300 metre square per gram of catalyst. That is the typical internal surface area which is available for the reaction in a catalyst pellet approximately of 3 millimetres in diameter, which is impregnated with the catalyst material.

Now, suppose let us say we want to calculate what is the bulk density. We can now estimate the bulk density which is essentially = the density of the catalyst into $1 - \phi$, where ϕ is the porosity. What is the typical density of catalyst? In fact, for the silica alumina catalyst the density is typically, typical range of density is about 400 kilogram per metre cube. And so now, we can convert this into grams and say this will be = 400 into 10 to the power of 3 into $1 - 0.3$ which is essentially = 280 into 10 power 3 gram per metre cube will be the density of the catalyst in grams per metre cube.

Now, what is the next thing we need? We need to essentially multiply the internal surface area which is available for reaction and the bulk density. So, let us do that. So, $S_a \rho_b$ is essentially = 300 into 280 into 10 to the power of 3, which is approximately = 84 into 10 power 6 metre square per metre cube. So, let us now compare this with the surface area which is available, the external surface area which is available.

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$$a_c = 1400 \frac{\text{m}^2}{\text{m}^3}$$
$$S_a \rho_b = 84 \times 10^6 \frac{\text{m}^2}{\text{m}^3}$$
$$S_a \rho_b \gg a_c$$

So, we noted that the external surface area a_c is essentially = 1400 metre square per metre cube. And the internal surface area multiplied by the bulk density is essentially = 84 into 10 to the power of 6 metre square per metre cube. Now, if you look at these numbers, one can actually see that the internal surface area which is available for the reaction to happen is typically much larger than the external surface area which is actually available for reaction.

So, the observation is that, $S_a \rho_b$ is typically much larger than the external surface area per unit volume of the reactor. And this is typically true for most of the catalyst pellet. The size of the catalyst pellet could be 1 mm higher or smaller. But irrespective of that, the internal surface area multiplied by the bulk density is usually much much larger than the external surface area per unit volume of the reactor that is available for reaction.

So, what we have seen in this lecture is, we essentially assumed that the external resistance to mass transport and the internal resistance to mass transport are actually comparable in a catalyst pellet. And as a result of which, what is controlling the overall rate of the reaction could be both the external resistance and the internal resistance. And we specifically started looking at a first order reaction where we want to now compare these 2 limitations.

We want to see how to estimate the overall rate at which the reaction is actually occurring when both the resistances are actually comparable. We also just wrote a simple balance where we compared the rate at which the transport happens from bulk to the surface should be = the overall rate at which the reaction happens in the catalyst pellet. And we put some numbers

and compared the actual surface area available for reaction within the catalyst pellet on the external surface.

In the next class, what we will do is, we will take this forward and we will compare the rates at which the reaction happens inside and the rate of transport and estimate an important quantity called the overall effectiveness factor and look at the implications of these. Thank you.