Chemical Reaction Engineering 2 (Heterogeneous Reactors)
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Lecture-25.
Isothermal Intraphase effectiveness factor Part-1.

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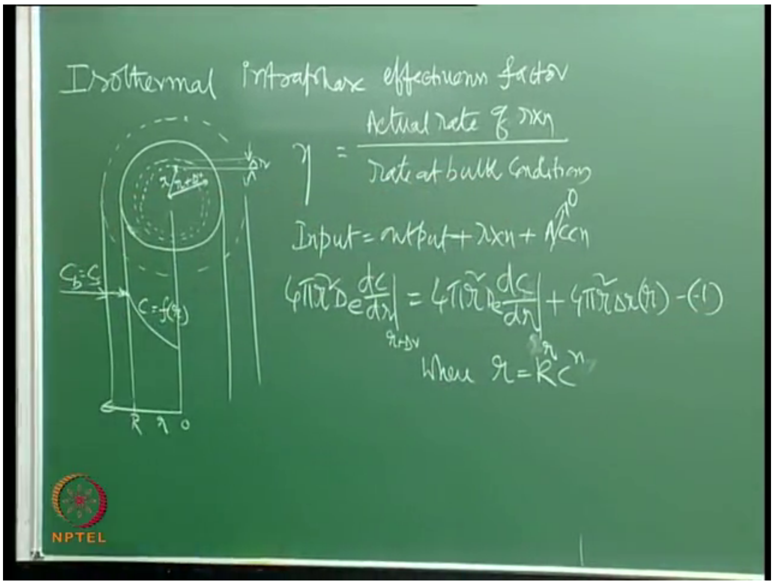


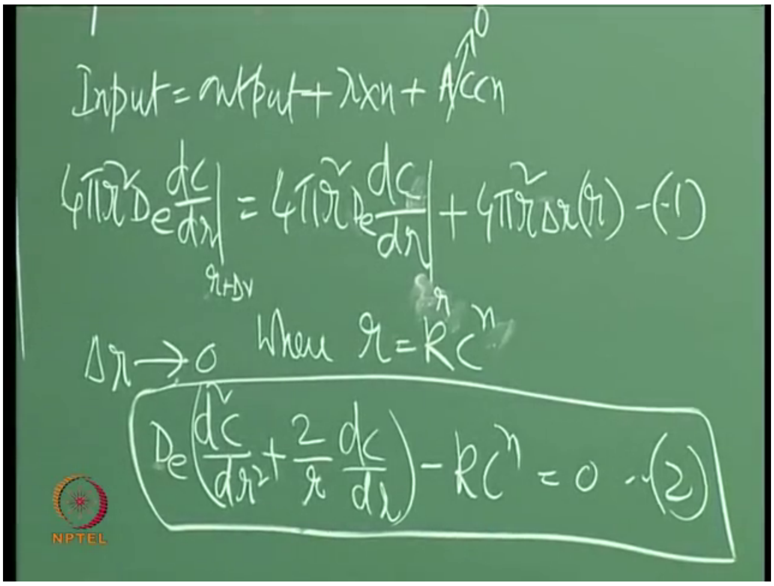
Isothermal intraphase effectiveness factor

$\eta = \dfrac{\text{Actual rate of rxn}}{\text{rate at bulk conditions}}$

Input = output + rxn + $\overset{0}{\text{Accn}}$

$4\pi r^2 D_e \frac{dc}{dr}\Big|_{r+\Delta r} = 4\pi r^2 D_e \frac{dc}{dr}\Big|_{r} + 4\pi r^2 \Delta r (r)$ -(1)

Where $r = kC^n$



Input = output + rxn + $\overset{0}{\text{Accn}}$

$4\pi r^2 D_e \frac{dc}{dr}\Big|_{r+\Delta r} = 4\pi r^2 D_e \frac{dc}{dr}\Big|_{r} + 4\pi r^2 \Delta r (r)$ -(1)

$\Delta r \to 0$ Where $r = kC^n$

$$\boxed{D_e\left(\frac{d^2c}{dr^2} + \frac{2}{r}\frac{dc}{dr}\right) - kC^n = 0 \quad ..(2)}$$

Professor: I think we have done the effectiveness factors for the external step, it is a film control. Now we will take the integral diffusion, pore diffusion step and then we will try to develop effectiveness factor for this. For we 1st anyway try isothermal as usual, isothermal intraphase effectiveness factor. I hope you understand, intraphase means inside the particle, okay. So we start with the diagram. That, of course there is a film outside, this is isothermal, so only one side is enough for me to draw, okay, so I will use this site. This is Cb, okay, also equal to CS because there is no film resistance, from then onwards it goes into the particle decreasing, okay.

So this C is a function of R where R is increasing like this, this is 0, R, Small r, Good. So what we have to now do is, the effectiveness factor definition, you know, yah Swami, what is 1 minus, yah, definition in words? Actual rate of reaction divided by, yah, actual rate of reaction divided by rate at bulk conditions, bulk conditions, CB, right, good. So here also we have to find out now what is the actual rate that is going on throughout the particle, that divided by, you have the rate based on bulk conditions, like for example you are talking about first-order reaction, then you have here, D into CV, okay.

Here the actual rate, that because C will be varying continuously, right. It is less than CV, isothermal, okay, this is less than CV, so of course temperature is constant throughout, CB is decreasing, I mean C inside the particular decreasing. The procedure is we should be able to 1st develop this profile, use this profile to find out how much A has entered into the particle, okay, let me tell a little story 1st. This we have to use to find out effectiveness factor, okay. CB I know I would bulk conditions, so if it is first-order reaction second-order reaction, K CB square, a CB or 0th order reaction, only K, so all these conditions are known to me here.

And here I do not know what is the actual red, so to find out that actual rate I have to 1st develop the concentration profile, okay. It is exactly like your mass transfer only, right. If I give you a concentration profile of mass transfer through any in the liquid or solid, then you find out what is the flux? I will simply give you concentration profile equation. C has a function of some constant into R squared Z, Z means you know that distance. Can you find out? How do you find out?

Student: (())(4:21).

Professor: DZ by… Yah dz by dr alone will not give anything (())(4:27), okay. That will give you the flux, that is the same concept what they are trying to use her. So the 1st thing is to develop the profile inside the particle and afterwards you differentiate that profile, evaluate at any place, maybe at r equal to capital R, right, that will tell you what is the flux that has entered into the particle, that will tell me that should have reacted under steady-state conditions, we are talking about steady-state conditions. So that will be the actual rate, that I substitute there, that equation, divided by rate at bulk conditions, if it is first-order, simply K into CB, cancel out you will get what is final, we notice eta.

So when you are deriving an equation for concentration of reactant into the particle, then you will get some other parameter what is called pie, Thiel modulus, okay. When you are solving the equation, as a dimensionless parameter. So the 1^{st} thing is to find out the concentration gradient. How do you find out the concentration gradient by the way? Where is the mass balance? We have to take a thin shell inside, this is r, this is r plus Delta r, Delta r is the thickness. Yah, Delta r is the thickness, that is Delta r. So now we will write what is entering into the shell, what is living the shell and what is reacting in the shell in steady-state conditions.

If you write that material balance, we have, okay, let me also writes this one, input equal to output, we are writing for A, if the reaction is for example A going to B. Output, reaction plus accumulation, all abbreviations, Rx and ACCn all that, accumulation. Because it is steady-state reaction, so this one will be 0, no accumulation, then her input is through the shell outside, we are taking the coordinate in the opposite direction, so plus we have 4 pie r square De dc by dr at r plus Delta r, r plus Delta r, that is outside. This is equal to, again 4 pie r square De dc by d r is at r, at r.

Plus we have the reaction steps when we have pie r square Delta r into r, rate, rate in the shell. Okay, if it is first-order, it is KC, so in general nth order also we can write. But this is actually nothing but r, rate of reaction in the shell. Right. So that can be simply K into CA, if it first-order. If it is Nth order, that is, equal to k into, where r equal to K C to the power of N, so this is equation on, so, this is not K to the power of r, yah, good. So now we will the limit as Delta r tending to 0, what you get the equation, which is familiar to you in many subjects, not only the subject, transport phenomena also is like this.

De d square C by d r square + 2 by r dc by dr minus, actually will get minus r, then that I will write as minus KC to the power of n, this is equal to 0, this equation is 2. So this is the differential equation which you have to solve for Nth order. And here that why was selling, you know my chemical engineers, you have to use a lot of mathematics. This R need not be only K Ca to the power of N, it can be also that KCa to the power of N divided by another K plus Ca to the power of N, whatever. Then you only go for solving this as numerical, yah, from numerical analysis, numerical techniques you have to use to find out concentration profile.

Using the concentration profile you have to find out actual rate, this rate anyway you will be knowing based on the bulk conditions, okay. So the procedure is universal but we are taking the simplest one to discuss many things during the, during the class because you will understand what is going on in the late, etc. Good, so this is a second-order differential equation, thing all of you will agree with that, okay, good.

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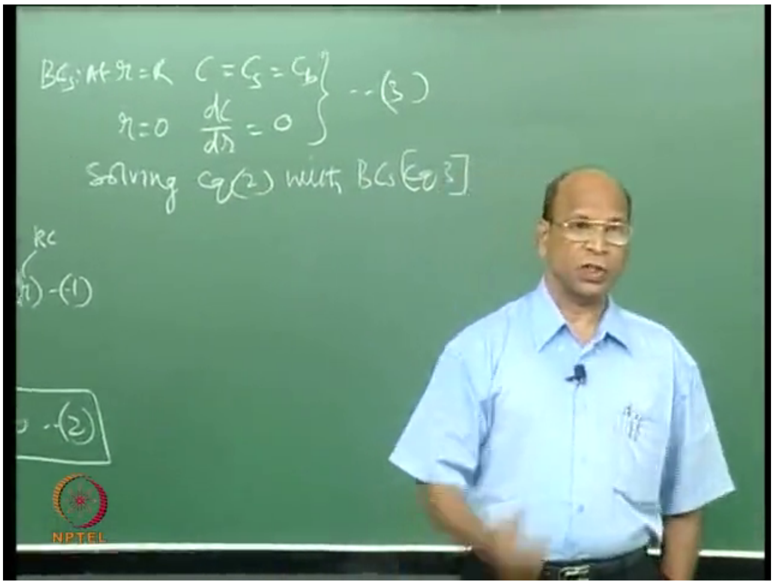

So then you need 2 boundary conditions. So what are the boundary conditions you can take there? r equal to, okay, this is, r equal to capital R, okay, at r equal to capital R, C equal to CS, this is also equal to CB, okay. Yah… Getting crash course ? Or particle is capital R, small r is the coordinate, small r is the coordinate. What you do in any problem, where we have distributed parameters system, we are using (())(11:20), inefficient is the change in space. Only beautiful systems is a mix flow reactor where there is no difference in concentration or temperature especially.

So that is called lumped parameter, all space, everywhere you see the same concentration, same temperature. So there you write normally, the balance in the input, that is inlet and outlet. Because you can see the change only in the inlet and then outlet, okay. Whereas in a distributed parameters system like a pipe where the reaction is going on, where there is no mixing, so that means that every point in the pipe along the line you will have change in temperature as well as change in concentration.

For that what we do is we take a small element like this, and then we write 1st what is really happening inside that, in this element. Then you will end up all the time with a differential equation. Okay. Why differential equation, because you are taking a differential volume and then trying to find out what will be the change in that and by using boundary conditions, these boundary conditions will give you, one is here, on the surface what is happening. The other boundary condition you need at the centre what is happening, okay, that means that entire Particle is covered because of the symmetry and entire thing is covered, right. So that is the procedure, you may not be knowing this procedure, so that is why am just trying to repeat, others also may not know but again you know once were I am just repeating that. Okay.

So what are the 2nd boundary conditions at r equal to 0? Dc by dr equal to…? What is happening? Why (())(13:16) there is no flux?

Student: Concentration is 0 at the Centre.

Professor: Why it is 0? At the centre always it is 0 no, concentration gradient is 0 or concentration is 0. Yah, good, concentration gradient is 0 but why so, is there any reason into that? You know the answer but I think correct point also is there, it is difficult for you maybe to imagine because we are assuming that we have symmetric diffusion from all sides, okay. That is why it is called also symmetric boundary conditions. If there is no symmetry in the particle you cannot say dc by dr equal to, dc by dr equal to 0 at Centre because it is, if we, if it is something often.

So because of the symmetric diffusion, okay, then dc by dr dc by dr at r equal to 0, that is another boundary conditions. I am not going to solve this, I will just finally give you what is the concentration profile but now you have to use all your mathematics knowledge, what you have taken in M Tech and B tech together, M Tech mathematics in chemical engineering also you have taken no? Idea of giving you that is to solve the problems. Okay, if I solved, if they solve, if you do not solve, then I think you do not solve. So that is the reason why we give some of these things to you and in the examination you cannot write that you know solving this you will get the final equation, you will not get any marks, I will tell you.

If you try solving that you will get concentration profile but I will write there, solving, using the boundary conditions, equation again solving these. There are many other beautiful techniques to solve this. Another point I want to tell you her, when I write this equation, okay, here you can say that let say for simplicity it is K into C for first-order. What should be the units of K, you should be very careful, it is a heterogeneous system. Heterogeneous reactions always you should be careful with the units, okay. Under these conditions where I have written the equation, what should be the value of K, I am in dimensions of K? Moles?

Student: Moles second.

Professor: KKK.

Student: Meter per second.

Professor: Meter per second, yah, okay, you substitute and tell me whether you get the same units. What are the units by the way here? It is a flux multiply by the area, so what do you get, mass flow rate or molar flowrate, okay. Yah, that is fine, okay, moles per second only you will get. Now put everywhere here, here, here, then tell me what should be the unit of K? Then why do you say meter per second. Okay, now I will ask (())(16:04), okay. Why do say it is per second, what is the assumption that, there is an assumption? Moles per second… Intensive rate, not extensive…

Student: (())(16:24) area of the particle.

Professor: What are the units of r?

Student: Moles per metres per second.

Professor: Yah, you now substitute moles per metre per second and then find out what is K. This is what is wrong, first-order reaction, k is timing was some might only is only strictly valid for homogenous or when you express the rate based on volume of the particle, volume of the particle. You see, how much discussion is unnecessarily required here. But I feel it is not unnecessarily required because I know your attention is not here. Not today, everyday and not, if I do not mention that, you will not even bother to think, you will not even bother to think.

And in examination they will have definitely doubt, why this fellow key is given as meter per second, this is what many many units, sometimes I can give even in you know, if the rate is based on moles per seconds per weight of the catalysts, then density of the catalyst will also come into K, density units, those things also will be there. So if you look into the literature in various books, so different books will give you different values for K, depending on how they have defined the rates. Because it is a catalytic rate, you can express based on surface area, you can express based on the catalyst of the particle, you express based on the whole bed volume, bed volume also, okay. So that is the reason why you may get different units for K value.

I think that is necessary, then definitely I have to tell you that. So now solving this equation 2, with BCs equation 3, BCs equation 3, okay, what you expect her age, concentration is the function of, you should expect no, Anand Kumar, what do you expect from this equation? What are the variables here? I am really asking you like a small child. Yah.

Student: It will be concentration…

Professor: Only one?

Student: Distance.

Professor: So what you get when you solve this? Concentration as a function of r with the parameter K and De. Now you could have got some idea this K by IDE is Thiele modulus for first-order reaction. Okay, because I have to divide whole thing by IDE, then you will have like in your normal format, where all of us learn the dy by dx Correct no. I do not know who started this dy by dx, all mathematics, 1st we learned differential equations. So that dy by dx form if you want to change, so this one will be d square y by dx square, X is r here, y is C there because many people are comfortable when you say dy by dx. The moment we say DC by dr, wind off, okay.

So that is why you have to convert this into the solvable differential equation by using even dimensionless quantities, okay, even this equation can be converted into dimensionless differential equation. Like taking for example DC by, what will be the logical parameter to non-dimensionalise CB, always C0 because I think transport phenomena effect, yah. Here C0 is CB, R, capital R, size of the particles. So when you use all that, you will get automatically the Thiele modulus, so please do that, please solve that.

It is not only this, I will give you later for slab. If you have a slab like this, whether the action is taking place this side, reaction is taking place this side and all these things are sealed for reaction. So any symmetric diffusion from this side, from this side, so you take half of the particle and then write the balance within that shell, like again, same, small shell, a differential equation, right, then take the boundary condition, solve, you get concentration as a function or, that is one cylindrical particle, okay. This side, the side, both are closed, not all, not available for reaction, another diffusion throughout, symmetric diffusion, now write the balance here.

If I look at this point, you will have a circle, within a circle you have the small volume, what you take, element, there you are again have to write symmetric diffusion. Take the corresponding boundary conditions, again you have to get a differential equation, take the boundary conditions and then finally you have to solve. These are really important, anything can be asked in surprise test, or in the final examination. Always I have to blackmail you with examination, otherwise simply forgotten. Good, yah.

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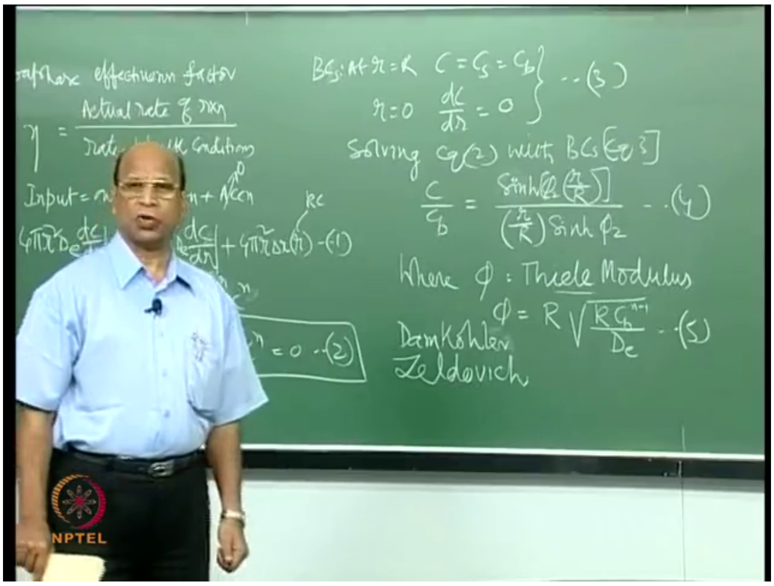

So anyway, so when I solve these, what you get here is C by CB, CB equal to CS, equal to, sin H, no, I think I will use another term here, phi 2, phi 2, this entire thing is sin H, sin H is there, hyperbolic function, sin H. This divided by r by Capital R sin H by 2, this is equation 4, where I will write generally phi, 2 will have some meaning for, 2 will give, it is a spherical particle and 1, phi 1 will be for cylinder, phi 0 will be for flat plate. Okay, so that is why we will just give that notation but in general where phi is Thiele modulus, Thiele modulus for Nth order reaction and is expressed as yah, expressed as R square root of K CB to the power of N minus1 by De, this is phi, okay, this is Thiele modulus.

Thiele is the name of that person who has proposed that. And in fact it is not fair enough to give credit to only Thiele. Thiele is from US, there was a person from again Germany, Dam Kohler, and another person in Russia, Zeldovich, all these 3 people simultaneously solved this problem in their own places. Because there was no Internet, nobody knows what they were doing at that time. These all happened in 1936, 38, 37, during that time, okay, all 3 of them. And but anyway, Americans will have always the loud mouth, so then they will get this, this name is given a Thiele modulus but other people also have worked on the same problem, diffusion reaction.

Who are the 3 people? Thiele is one, Dam Kohler, and Zeldovich, all the 3 people, okay, good. There is also sometimes, history also is required, okay, good. So this is the one and, yah, you can also beautifully plot this C by CB versus R by r as a function of phi because phi is the only function there. Function is a Thiele modulus, but anyway. This is, when I say it is Thiele modulus, is there any physical significance of this Thiele modulus? Let us say I will say Thiele modulus I have 200, what is the meaning?

Student: (())(25:47).

Professor: So which is controlling?

Student: (())(25:54).

Professor: Yah, diffusion control. That means diffusion is very very small in the denominator, so reaction rate must be high, so phi 2 is large value, phi is large value, so that is why large values of phi means we have mass transfer through the coarse controlling, right. Similarly it is 0.1 or less than 1 or maybe 0.01, very small values, phi values. So then diffusion is very very large but the reaction, that is K value, that is small, so that this controlling, okay. So these things like Reynolds number, it will always give you some idea, okay, diffusion, I mean Thiele modulus very large, usually it is 10, beyond 10, 100 definitely you are in very very strong diffusion of regime, very very strong diffusion of regime.

The effectiveness factor will fall down to even 0.1, 0.5, 0.01, okay, that means only 1 percent of the surface area is used for… Yah, it is really funny also. When only 1 percent of the surface is used, the reaction is very fast. Read more? On the reaction is so fast, that the moment all the particles, all the reactants, all the reactant molecules will come to the surface,, it is converted. So it is not even allowing that to go inside the post. But on the other hand if you are able to push more and more inside, then you will have very very high (())(27:29), because it is very high, okay.

If you are able to push, but that will not happen most of the times, that is why very active catalysts, very active catalysts like that in a more noble metals, okay, these are only distributed on a support but not used as single particle. Why, do you know the reason? Because all these catalysts are very very fast, so that is why you and most of the time even if you take a particle, only outside surface area is used, the remaining internal surface areas, internal material is totally waste.

Platinum is very costly, okay, so that is a reason why you now take this Platinum, try to deposit and a support like silica, activated carbon, uniformly throughout the particle in a porous particle. So then depending on the pore size, you will have, the reactant gases, you will have to find out that, the design of the particle. So then you will allow more and more gas inside, so then entire particle coated with these noble metals will be used. Okay, good. So that is why I think you know you can also nicely plot ensure how the concentration profiles look like and I think I will do that in a small graph.

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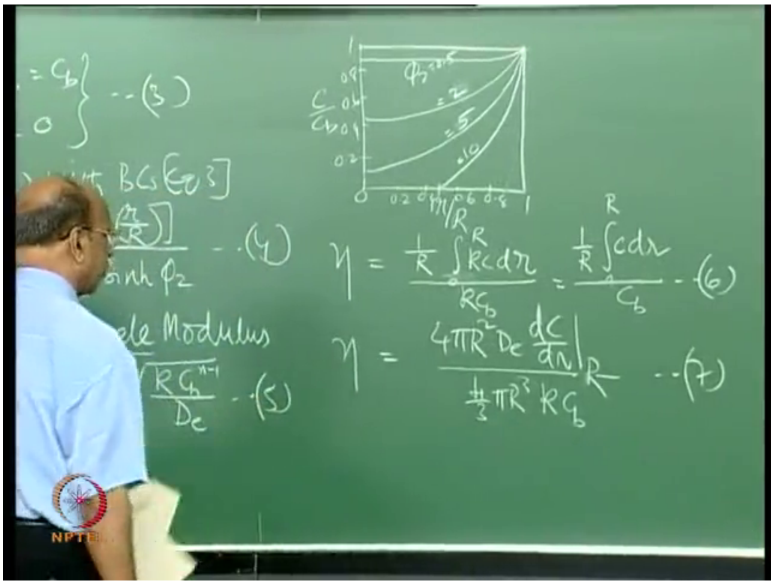

This is C by CB versus r by R, this is the advantage of having dimensionless numbers, dimensionless variables. Then I have your 0.2, 0.4, 0.6, 0.8, 1. 0.2, 0.4, 0.6, 0.8, okay, good. So now the parameter is phi, okay, if phi is very small, how the curve will look like? You should have some expectations so? Come on, come on, I thought I will do many things but… Yeah, Kartik, any ideas? Like this, where it starts, where it ends? He is selling like this, Reebok or Nike? Nike or Reebok?

Student: Nike.

Professor: Nike, yah… What you are thinking? What is that? Where to start, where it will end?

Student: It will start at 1 and…

Professor: Yet, starting from 1, that is one, with difficulty. Kaavya? Think. From where to where? You are starting, then you have to show the endpoint. It is a dimensionless coordinate, what you are trying is nothing but this concentration profile, right. Where it has to start?

Student: From 1.

Professor: Okay, yes because r by R is that, okay. So that means it has to start from you, now tell me how does that go? If it is very very low, then you may get like this, okay, if it is slightly larger, you may get like this, more larger like this, like this. So for example this may be phi 2 equal to maybe 0.5, 1, 5, 10 or this may be or okay I can also, maybe this is correct, 5, 10. 100 means like that, so what is the meaning? You tell me the meaning for 10.

Student: (())(32:37).

Professor: Before it is going into the particle, maybe around 50 percent of the particle only is occupied by the gas. Why, by diffusion limitation reaction is possible. If it is 100, almost near, this much, so this is her. Why, mass transfer limitation, reaction is very fast. Beautifully one can predict, I mean develop that kind of interest I see. So many times I am telling you instead of seeing Google, you should take pen and paper and start trying these kind of things and just imagine what is happening in the process and then try to write. Then automatically mathematical can write and then check whether you are right or wrong. Anyway, in the examination I can ask you, if you are not bringing the assignment and all that.

So draw the profiles, do not scold me at that time. I will give you graph paper, pencil I will not give you, okay, so then you have to calculate and you have to draw the profiles and explain what is the meaning of 10, 5, 2 and 0.5. If it is 0.1, you may get almost here. What is the meaning? Reaction control, the entire particle is now occupied by the gas, so entire surface area is used for the rate of reaction or the reaction to go on time. Wonderful points, good, okay. So now, once you understand the concentration profiles, now we have to take on concentration profile, is this is the concentration profile at particular conditions given here in the, in this, when you are writing the balance.

And now you have to differentiate this at r equal to capital R, this equation, dc by dr at r equal to capital R and then multiply that one with De, that will give you the flux like here, okay. But you are evaluating at r equal to R, multiplied by the and 4 pie r squared also and then rate at bulk, then he will get effectiveness factor. Because you using simply these definitions, this definition of effectiveness factor is, actual rate divided by rate at bulk conditions. Now actual rate is what? Because the concentration is changing at each and every point, you have to either integrate or differentiate, one of the things.

So that is why I can give you 2 methods eta can be now found from actual reaction rate as 1 by R 0 to R, yeah 0 to capital R KC dr divided by K CB. If I cancel, isothermal, if I cancel this and this K out, what the equation we will get? I can also write a 1 by R integral 0 to R c dr by CB. It is just nothing but concentration average, integration throughout. Okay, some kind of average in this, right. So that is the actual rate because KC is the rate, KC is a rate, K CB is the rate, okay. So this is one method, the other method is this also can be written as 4 Pie R square De dc by dr at capital R, that is the flux multiplied by 4 Pie R square will give you the rate.

This divided by 4 by 3 Pie R cube K CB, this is 5, this is 6, that is equation 7. Any one method can be used, both are same, right. Here why did we use 4 by 3 R cube and 4 Pie R square? Because that K is expressed based on volume of the particle. Okay. Good. So please do that, this I am not doing again, this differentiation or integration, anyone method you can use.

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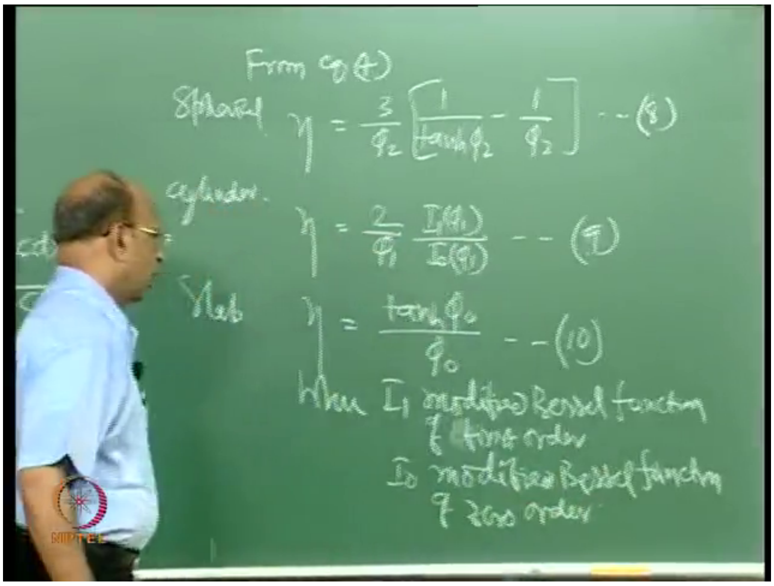

And then what you get, if we substitute, let us say from equation 7, that is easy for me normally. Eta will be 3 by phi 2, 1 by tanh phi 2 - 1 by phi 2, so this is equation 8. This is for spherical particle, this is what we had started. If you do the same exercise for cylindrical particle, for cylinder, eta will be 2 by phi 1, this is equation 9, for slab eta is tanh phi 0 by phi 0, so this is equation 10. And anyone remember what is that I1, I 0? You said, who said that? How do you know?

Student: (())(38:55).

Professor: Who is teaching multiphase? Yeah, this is Bessel function. When did you get that? Effectiveness factor also you are doing that, something else. Yah, so in this equation, you know d square C by dr Square +1 by r you will get for, 2 by r for spherical particle, right, 1 by r for cylinder. So you do not have a solution except you know you have to go for this Bessel functions and I1 is a modified Bessel function of first-order. I0 is modified Bessel function of 0th order. Okay. I have to write here, all the things you know, where I1 is modified Bessel function of first-order, okay.

And I0 is modified Bessel function of zero order. What you have to do is when this kind of problem is given? If I ask you to calculate what is effectiveness factor, you have to go to mathematical tables, okay. So in the mathematical tables you have to calculate phi or phi 1 here and then go there, correspondingly substitute in that constant and then get the corresponding values. Okay. Good. So this is the one for 3 geometry. You have class no, so I think I have to stop here. You have to draw the figures and all that later.