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Lecture - 10 Intra-particle diffusion: Thiele modulus and effectiveness factor Part-I

Good morning. So, in the last lecture we looked at how to incorporate effectiveness or rather effective diffusivity or poor diffusion effects on the reaction kinetics. We again I will repeat like we have the reaction taking place in six steps. First is an external mass transfer of the reactant; then internal diffusion, adsorption, reaction, desorption of the product, internal diffusion, back diffusion on the product and then the back external mass transfer of the product. So, out of which we have already considered three steps adsorption, reaction and desorption. Now, we are trying to incorporate the effect of internal diffusion.

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So, we have these catalyst particles and we are looking at the diffusion inside and this is external surface r is equal to capital R and this is centre. I told you in last lecture that it is a porous particle; you have pores actual moment on the particle will be tortuous. But all these effects there constriction, tortuosity, porosity everything is incorporated in a term called effective diffusivity, D e effective diffusivity and when we write when we use this term effective diffusivity; then you are free to write normal fix law for diffusion in the radial crop coordinates if the particle is spherical.

So, in that case the flux becomes D e into d C by or dC A by dr of course, the minus sign. So, this becomes a flux now what is a difference between this flux and flux that is taking place in a non-porous particle or other not non-porous or is a continuous medium rather is a continuous medium the d is a different diffusivity is a bulk diffusivity that we talk about normally. There is no effect of porosity; there is no effect of walls; no effect of tortuosity as well.

So, this is a diffusion that is taking place in a radial coordinate, but then we are incorporate in the effect of the solid matrix there, the porosity material effects. So, D e takes into consideration all those effects, and then I can write as if it is continuous medium inside a particle; we are already discussed this at the length in the last lecture. Now, what are the equations; because if like why what we are done it trying to do here is to get a concentration profile inside a particle?

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Now, we define dimensionless concentration psi is equal to C A divided by C A s the this is the external surface concentration it can be C A b as well. So, I can use these terms sometimes like either C A B that is bulk concentration on C as that is an external surface concentration. Because right now we not considering external mass transfer effects. So, this is psi and then there is this lambda which is nothing but r by capital R, r is a radial distance; capital R is the sphere radius.

Now, if you do this I get an equation for the concentration dimensionless concentration as d 2 psi by d lambda square plus 2 by lambda d psi by d lambda minus psi not psi phi n square remember this psi raised to n is equal to zero. What is this? This is a very important term this is very important term that tells you how important the pore diffusion effect are. Now, we call this as a Thiele modulus.

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Now, Thiele modulus is given by phi n square k n s a rho c R square C A s raised to n minus 1 divided by D e. So, we know the meaning of in each and every term here, k n is the rate constant permanent area permanent area, n denotes the order of the reaction and define it for the order here n; s a surface area permit way to the catalyst, rho c is the density of the catalyst mass per unit volume. So, this entire quantity can rho c is rate constant per unit volume this is per unit area. This is per unit this two together per unit weight and this three together per unit volume of the catalyst.

Then, we have these terms this is a radius then your concentration order and effective diffusivity. This, we can further simplify this or rather further play with this particular expression and show that phi is the ratio of the intrinsic rate to the diffusion rate. So, it represents the relative magnitudes of intrinsic reaction rate and diffusion rate and if value phi is very large value of phi is very large in that case the diffusion resistance is

significant. So, Thiele modulus if it is significant substantial value this is very high value, diffusion effect we cannot neglect them.

On the other side, if you have phi value very small say 0.0001 in that case diffusivity effective diffusivity is likely to be very large compare to the intrinsic reaction rate or the rate of the reaction or rate constant is very small. So, that its diffusion is not important at all; it is like open surface or the particle or the molecules are getting access to every side without any problem, concentration gradient inside a particle is negligible. It is almost a flat profile. So, that is a meaning of phi.

So, now let us try and solve this equation now we go further because we want to see the concentration profile and why we want concentration profile is to further calculate over all reaction rates; because you not yet got an expression for the reaction of the rate to be used in reacted design. So, we are heading towards it. So, this is an equation and this is a meaning of psi n boundary conditions, we already looked at boundary condition in terms of concentrations dimension concentration. Now, let us write then in terms of nondimensional concentration. So, psi is finite where at lambda equal to 0 very important at the centres size finite or d psi by the d lambda is equal to 0; d psi by d lambda is equal to $\overline{0}$.

Then, next psi is equal to 1 at lambda is equal to 1, why because at external surface at external surface lambda is equal to 1; r is equal to capital R and psi is equal to 1 because C A is equal to C A s. So, lambda is equal to 1 here lambda is C A by c s. So, we have these deferential equations with these boundary conditions. I mean to solve this equation not so easy, but there are ways to work with it. So, if you assume reaction to be say first order reaction solve it analytically.

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First, we have a variable called say y which is defined as psi into lambda; now, if you do that and substitute for it in this equation; then you can do some mathematical jugglery and get an equation in terms of y and lambda like this. So, d 2 y by d lambda square minus phi 1 square y is equal to 0. Now, y 1 here because order is one; so, this n here represents the order. So, I am writing it for a first order reaction I am writing it a for first order reaction I am making assumption that y is equal to psi into lambda; the product of these two variables.

So, what happens is I can get rid of psi here you can write dy by d lambda this definition with respective lambda and then substitute here. You can do that mathematical manipulation I what you get is this and this is very simple equation to solve. There is a solution for this equation the general solution for this equation, which can be given as y is equal to A 1 cosh phi 1 lambda; this is mathematics B 1 sinh phi 1 lambda.

So, this a general solution for this equation with a boundary conditions of course, I have not applied those boundary conditions yet because now I have the equation in terms of two constants A 1 and B 1, which has to be found out with the help of boundary conditions and you know meaning of phi 1 and lambda. So, what is y? y is psi into lambda. So, let substitute for y now and I get my equation that I want because y is a dummy variable there.

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 $\frac{1}{\sqrt{2}}$ sinh

So, substitute for y; so, what you get is psi is equal to A 1 divided by lambda cosh phi 1 into lambda plus B 1 divided by lambda sinh phi 1 lambda. Now, we have to make use the boundary conditions to get value A 1 and B 1. So, let us talk about the first boundary condition, where at lambda is equal to 0 at lambda is equal to 0 lambda is equal to 0 you have psi finite. Now, look at this equation if this is lambda if lambda is equal to 0 then of course, this factor because of zeros sinh do not you worry much about it, but then here this becomes 0.

This term is finite why because cosh 0 tends to 1 when lambda becomes 0. So, this is 1 this is 0 this is finite this term off course taken care of because this is 0 this is 0 probably you do not have to worry much about it, but if this is 0 this is yeah if this entire term is tending to 1; this is zero. If I am saying that this is finite then what should be the value of A 1 is quite obvious; if A 1 is finite A 1 is finite then this becomes infinite because this is 0. But this is finite. So, this is not true. So, A cannot be finite means A 1 is zero. So, that implies A 1 is 0 I will repeat this tells to this is cosh become one this become 0; this is finite; this is any way 0 by 0 tending to 0 by zero; that means, this is this term is finite.

But, then if A 1 is not finite then this would becoming infinite that is not correct because psi finite. So; that means, that A 1 has to be 0 it cannot be any finite number. So, one once A 1 become 0 I can get a value of B 1 from another boundary conditions. So, let me first psi is equal to B 1 by lambda sin h phi 1 phi one into lambda. So, let us apply the second boundary condition.

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What is that second boundary condition? Second boundary condition is the one where you have at lambda is equal to 1 psi is equal to 1. So, this equation gives me the value of B 1, what is the value of B 1. So, 1 is equal to B 1 divided by lambda sin h phi 1. Now, B 1 is nothing, but which implies B 1 is equal to lambda divided by sinh phi 1. So, if you substitute for all the value of B 1 in this then I get a final expression in the form psi is equal to which is nothing,,, but C A divided by C A s we already defined it which is equal to 1 by lambda sinh phi 1 psi divided by sinh phi 1.

So, this is the concentration profile this is the concentration profile that we want it of course, for the first order reaction. For the first order reaction look at this phi 1 first order reaction because it was easy for me to solve for this solve equation for first order reaction. How am I going to use this see this is lambda the way have shown lambda here it look looks like tau, but actually its lambda. So, this is the equation for concentration profile I can substitute for lambda r small r divided by capital R and get the equation in dimensional form C A between C A and small r.

That gives me the concentration profile inside a particle. Now before we go ahead and define certain parameters later. We will look at a profile how it looks like; now we can always qualitatively draw a profile concentration profile from this equation. In fact, we do not need equation initially to just imagine or rather guess the profile inside a particle.

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How will it look like you have r increasing in direction; that means, r is equal to 0 here r is equal to capital R here. Then, you have this concentration or you can write psi C A by C A s is better we do that because in then I can I know what is the maximum value that is one. Now, this distance as I go from centre to the external surface how will it look like, where exactly it is going to maximum is going to maximum at the external surface at external surface is going to be 1 here because it is C A is equal to C A s here and inside. So, this is where I have bulk and particle started from here and it goes towards a centre this concentration is going to go down.

So, typical concentration profile is going to be like this and at r is equal to 0 at r is equal to 0 at centre dC A by dr or d psi by dr is zero. So, it going to be flat so, it going to be flat look at this at this condition is satisfied its finite, but dC A by dr is going to be zero symmetry. So, this is a typical profile that I am going to see this typical profile that I am going to see is inside a particle. Now, this profile will depend on which parameter this profile will depend on just one parameter; look at it differential equation there is one dimension this number that define everything inside the catalyst which is nothing, but Thiele modulus phi n for n th order reaction phi 1 for first order reaction.

Depending on the magnitude of phi this profile will change qualitatively it will look like this. But you can imagine now tell me if value of phi is very, very small, what does it mean; value of phi is very small means that the concentration variation inside a particle is negligible. The profile is flat; there are no gradients why because there is no pore diffusion effect. The pore diffusion is so, fast that a particle before the sorry not particle molecules before they react they immediately get into the inside a pores and inside a particle and somehow the concentration is levelled off. It is exactly on which is quite close to what you had in external surface.

So, for phi is very, very small values of phi this profile is flat this is very small value of phi. So, let us say phi 1 or phi let me call general value phi n, which is very, very small. This is some intermediate value of phi and it value of phi is very large then the gradients are significant. Then, you can imagine something like this. This is for phi n very, very large very large value of phi n or phi 1 whatever it depending on order of reaction. Importance of pore diffusion how it changes and how this characterizes into the one parameter, which tells you about importance of pores diffusion that is phi.

Pore diffusion effect, you should remember this no pore diffusion effects this is the one somewhere in between both are important reaction and pore diffusion; I cannot neglect both of them. But suppose I am dealing with case like this then pore diffusion can be ignored whatever excise we have done so far Thiele modulus. Of course, you have to calculate it first to know whether it is important a lot, but then later on do not have to worry about profile inside reaction taking place external surface concentration.

You design your reactor like what you do for normal case, but then from for a catalysis person you should thing why even if. So, it like this he has prepared a good catalyst say platinum on alumina and he has nice porous catalyst with very large surface area. It is nicely dispersed; that means, its concentration uniform everywhere inside a catalyst particle everywhere inside a catalyst particle the concentration of p t is uniform; what is p t platinum and I am using alumina as a support and platinum species are nicely distribute inside.

Now, imagine if value of phi is very, very large a situation like this, is it a good catalyst? No, why because the platinum particles somewhere in the core somewhere in the core that is near the centre are not seeing reactant molecules at all. Because you see the profile here this flat and almost zero concentration all of reactant molecules are somewhere near external surface. So, what is use of putting platinum there is useless. Unnecessarily, I am taking efforts on preparing the catalyst dispersing it very well, but some of the platinum species or the sized are in accessible why it happen, because effective diffusivity is very small.

Why effective diffusivity is very small look at an expression of effective diffusivity bulk diffusivity into porosity that in diffusivity into porosity into constriction factor divided by tortuosity. So, if the tortuosity is very, very large effective diffusivity will go down if the porosity is very small pore diameter that maters; the pore diameter is small effects will be significance. So, I had needed to design a catalyst now such that I get rid of the pore diffusion effects. So, that this platinum is accessible or otherwise if I am happy with the platinum that I have put at a surface here and reactions taking place in the rate that I want then do not do this do not take efforts on dispersing the catalyst nicely.

Just put a catalyst only in the exterior the part where it is very close to external surface only this part. So, that is the meaning of it to this analysis helps the catalysis person the catalysis or the person who designs the catalyst very well. So, in this we have knowledge of pore diffusion effects. So, that is the meaning of all these. So, let us go ahead now we understood how the concentration changes inside a particle we are going to make use of this and a get a rate equation that we want for the reactor design. See the ultimate aim is to design a reactor ultimate aim is to design a reactor.

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So, before you go ahead. So, let us go back to CSTR suppose I was CSTR in that I have this catalyst particles remember, what did I write F A 0 minus F A plus r A into W is equal to 0, W is a weight of the catalyst. I express some time I put a dash here if you see notation in use; r A dash it is per unit weight of the catalyst. Now, this equation I told you last time before we started our discussion on diffusion effects this term is nothing, but the one that is obtained from the Langmuir Hinshelwood mechanism or Eley-Rideal mechanism whatever taking into consideration adsorption desorption reaction.

So, this particular term now what we looking at are how this term going is going to get modified if you have pore diffusion effects also present. So, that is the exercise we are doing say this is a design exercise; I am just taking about CSTR it can applied the flow reactor as well. But then what is the objective of this entire excise we will do is look at this particular parameter in the rate of reaction. This variable how does it change now; how do in incorporate effects of pore diffusion effects pores diffusion.

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So, let us go ahead I have this equation concentration profile psi is equal to C A divided by C A s is equal to 1 by lambda sin phi 1 lambda divided by sinh phi 1 for the first order reaction. Now, I am going to define a factor which is very, very important and is going to help us later a lot for the reacted design. So, what is that factor, which is effectiveness factor? So, let me call this is effectiveness factor and I am going to define this first and then get an expression for it. This is a effectiveness factor as a name says it tells me how effective is a catalyst how effective is the catalyst.

Now, I am this particular factor is going to incorporate effect of pore diffusions if the effectiveness is very large; that means, pore diffusion effects are insignificant if the effectiveness is less than the pore diffusion effects are more. So, it works exactly opposite to Thiele modulus. Thiele modulus means if the effectiveness if Thiele modulus is large then the pore diffusion effects is significant resistance is significant; if Thiele modulus is small the resistance is small, whereas effectiveness factor is exactly opposite. So, we are going to see an inverse relationship between this two; eta and phi that relationship is going to be inverse not so, striate forward will see how it works.

This an advantage you may ask me why your defining two parameters another parameter. So, it will be clear as I when we go on solve equations later because effectiveness factor tells you many things, which are like quickly you can estimate the importance. Now phi value you can vary from 0 to infinity, whereas effectiveness factor will varies from zero to one and some time it can be greater than one will talk about it. Now, this effectiveness factor is nothing but now listen to me carefully this is the observed rate this is the observed rate, this is the observed rate of the reaction or actual rate observed or actual rate.

That means if I do experiments whatever rate I get divided by, now this is very important the rate calculated at external surface rate calculated at external surface conditions. How do we calculate rate external surface? What do we need to calculate the rate external surface? You need external so, you need concentration. So, this concentration is not a concentration is inside, but the external surface concentration in our case it is C A s or C A b whatever you need temperature also we not talking about knowledge of thermal reactions so far.

But then later on we will talk about that as well. So, I am just calculating rate at the external conditions it can be concentration it can be temperature because for rate calculation I need temperature also because rate constant is function of temperature. So, I am calculating of an external surface; what does it mean let me write it down in words because this is concept is quiet important.

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Let me write down in words; rate calculated at the external surface. It means that lets assume let us consider a hypothetical situation, where you have the surface which is present inside a catalyst the surface, which is present in inside a catalyst is opened up to the external environment to the external environment. So, this is a C A s what was happening before that there was a diffusion taking place some of the side inside we are seeing less concentration then external surface concentration, now I am imagining a situation where entire surface opened up.

So, let it be saying five hundred meters square per gram; let it be football ground whatever large external surface, but which is open to the external conditions. So, that C A s the all the sides on the surface we are going to see this. So, the rate calculated under those conditions for this concentrations is going to much larger compared to what it would be when calculated for inside particle; when the concentration goes down in the presence of pore diffusion effects. So, the rate here is smaller because a concentration is less, whereas a rate here is large because all the sides are seeing higher concentration or larger concentration, which is there in the external surface. So, imagine two scenarios.

So, what I am doing is I am comparing this with this. So, rate calculated at the external surface is nothing, but rate when the area or all the catalytic species this exposed to the external condition conditions means C A s and T s, I hope this clear I am comparing these two scenarios compare in the sense so through eta. So, eta now eta is rate for this divided by rate for this and this rate is going to be smaller. Most of the cases they are exception situation, where this height is higher will come back come to that. But otherwise normal situation this rate is smaller than this rate. So, I am going to see the value of eta to be less than one. So, value of eta is less than one.

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Now, eta is r A since it is reactant let me called as minus r A divided by minus r A at surface minus r A at surface. So, it depends like it per unit volume it is per minute weight it can be r A dash divided minus r A dash it is all unit. So, that is not mater so, dash is taking care of per unit area. Then there is another thing called as per unit per unit surface per unit surface, per unit volume per unit weight per unit surface it will be other way around. It would be per unit volume, per unit weight and per unit area so whatever. So, what we are doing here is we are looking at the rate which is observed rate actual rate divided by rate calculated at the external surface.

So, we can say that let us take this particular ratio that is minus r A dash, which is per unit weight of catalyst into mass of the catalyst divided by minus r A dash s into mass of the catalyst. What is the unit of this? This is per unit way to the catalyst into weight. So, it is the unit is going to be moles per second divided by moles per second. So, I am going to evaluate this or get an expression for this in terms of moles per seconds and substitute here and get a value of eta. So, let us try and get a numerator first. So, let me call this is M A divided by M A s that is moles per second reaction rate actual reaction rate divided by moles per second reaction rate calculated at an external surface.

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MAS = Rate per eint Axa
X Sent-Axa, x Mas.
X mass of cat.

So, let us get an expression for M A let us get an expression for M A that is or other M A s first that easy to understand that is calculated external surface. So, it is rate per unit area into surface area per mass of the catalyst into mass of the catalyst. So, rate per unit area is unit surface area is say k rate constant into C A s, I am calculating at external surface; so, C A s into surface area s a in terms of density mass of the catalysis rho c into fourthirds pi R cube. So, this is M A s and I am going to use this later.

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Now, let us look at M A a let us look at M A. I will bring back this particular slide again. What is M A? M A is the observed rate. Now how do I calculate the observed rate? Now I know the concentration profiles inside a catalyst; let us assume first order reaction. Now, I know that psi is equal to whatever let sinh phi 1lambda divided by sinh phi 1. So, that concentration profile I know. Now, you have this catalyst particle inside, which there is a concentration gradient and then I know what a gradient at an external surface is. So, if I am sitting at an external surface I know, how many molecules are going inside; how many molecules are going inside at steady state there is no accumulation inside.

So, if I am at the external surface and just watching number of molecule going inside a particle calculate a rate there calculate flux there then that is nothing, but rate of reaction. Because whatever happening inside the gradient that is generated will is based on the reaction that is taking place inside. It is because a reaction takes place inside that you have a gradient that you have the radiant inside it is because of the reaction. So, I am taking into effect or taking into account effect of reaction. So, if I am sitting here and just observing number of molecules going inside then it is a rate of the reaction.

So, how do I quantify it how do I quantify it quantify it is nothing, but a flux at the external surface into area into the area. What is the area? Area is this external surface area and flux relational surface. So, it is nothing, but 4 pi R square D e into dC A s by dr or the dimensionless if I just want to get a gradient in a in terms of psi that we have defined earlier it is going to be, d psi d lambda at lambda is equal to 1; now here it should be C A and add the external surface that is r is equal to capital R. So, I have this particular expression for the actual rate. So, this is the actual rate number of molecule going inside per minute time.

What is the unit of D e into e into dC A by dr? This is moles per second per meter square per area and I am multiplying it by area. So, the unit is moles per time, let me write it. So, this has unit moles per meter cube that is concentration into meter that is radius. This is unit of dC A by dr. What is unit of D e? Unit of D e is meter square per second. So, what is the unit of this product moles per this meter square into second and if multiplied by area which you have r square meter square; so, moles per second unit of this entire this thing moles per seconds unit of M A, that is what I want.

So, look at an expression for eta that we have got. So, this is eta. So, eta is M A divided by M A s and this is nothing, but moles per second divided by moles per second. So, I got an expression form M A and M A s. So, I am just going to substitute for M A and M A s in eta and see what I have get.

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See. τ

So, eta is equal to M A that is 4 phi R square C A s d divided by M A s k 1 C A s s a rho c four-thirds phi R cube. So, this is eta now I get an expression of for eta if I know this and this is something that I have already calculated on other I know d psi by d lambda. I substitute for lambda is equal to one and I get expression for this. So, how do I get that psi nothing, but 1 by lambda sinh phi 1 lambda divided by sinh phi 1. This can give me d psi by d lambda and if I substitute for lambda is equal to 1.

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What I get is, d psi by d lambda at lambda is equal to 1 is equal to phi 1 $($ $)$ phi 1 minus 1; phi 1 is Thiele modulus for the first order reaction. You can you can do it a mathematical jugglery. You have you can get a value of d psi by d lambda at lambda equal to 1; substitute for this in the expression for the effectiveness factor. Substitute for this in the expression for the effectiveness factor here, what do you get is going to be big expression, but easy to understand just doing it systematically.

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\gamma = \frac{4\pi R P_e G_{fs} (d_{fs} G_{rb} h d_{fs} - 1)}{k_1 S a S_e R^3 (d_{gs} m)}
$$

= 3. $\frac{1}{k_1 S a S_e R^2 / D_e}$. $\phi_{fs} G_{rb} d_{rs}$
 $\phi_{fs} = \frac{3}{\phi_1^2} (\phi_{fs} G_{rb} h d_{fs} - 1)$

So, you know the meaning of each and every term there. So, eta is equal to 4 pi R D e C A s phi 1 coth phi 1 minus 1 divided by k 1 s a rho c four-thirds phi r cube that is it. So, this is the expression for eta. Now, let me just play with this 3 into 1 divided by k 1 s a rho c R square divided by D e into phi 1 coth phi 1 minus 1 and this what is this this is nothing, but the thiele modulus. So, I have eta equal to 3 divided by phi 1 square into phi 1 coth phi 1 minus 1. So, I have got the expression for eta in terms of phi.

This is what I wanted, I told you there is relationship between phi and eta and this is slightly complicated relationship we will continue with this in the next lecture and I will tell you more about it. But remember as phi increases theta eta decreases; effectiveness factor is more means catalysis effective for porosity pore diffusion effects are less. So, we will continue with this in the next lecture.

Thanks.