Chemical Reactions Engineering II Prof Sanjay Mahajani Department of Chemical Engineering Indian Institute of Technology

Lecture - 12 Intra-particle diffusion: Thiele modulus and effectiveness factor Part – III

Good morning. So, we will continue a discussion on effectiveness factor. Now, today we like to wind up this particular topic. We have already looked at what is effectiveness factor. It is something that tells you the effect of pore diffusion resistance on the overall rate of the reaction. It is related to a dimensionless number called as Thiele modulus this is inverse relationship between eta and phi; eta is effectiveness factor phi is dimensionless number that is Thiele modulus. And effectiveness factor normally varies between 0 and 1.

But, there are some unusual or some exceptional cases, where effectiveness factor can be greater than 1, so what is effectiveness factor? In general effectiveness factor is the rate of the reaction observed rate of the reaction which may be hampered by the pore diffusion divided by the rate of the reaction that is calculated at a external surface, as if there is no inter particle pore diffusion resistance.

So, most of the time it is less than 1 because there is some resistance, if at all there is no resistance it is 1. But which are the situations where we come across in case where like the rate inside a particle becomes greater than overall rate of course, average on the entire particle radius the rate is greater than the rate that is calculated based on the external conditions?

Exothermic

So, I told you towards a end of the last lecture that eta can be greater than 1. When? It happens mostly in the case of exothermic reactions when in the particle the temperature inside and temperature outside. So, Ti is greater than Ts. When does that happen? It happens when you have exothermic reaction the heat is librated because of the reaction take place inside a particle old diffusion resistance is significant. So, it does not take place only at external surface, it goes inside reactant and another reaction take place and the heat is librated.

Now, this is another condition that once the heat is librated temperature will rise, but then if the heat gets dissipated fast from interior part of the catalyst particle to the external part. Then this dissipation rate will allow temperature to go down or come down to certain particular level and probably it will be equal to the external temperature. But if the dissipation rate is relatively low in that case temperature inside is going to go up and when that happens this is all that steady state.

When will that happen? If it happen when the conductivity the thermal conductivity of the particle now this again effective thermal conductivity like effective diffusivity because the pores structure. So, the thermal conductivity on particle is less than the ... or it is relatively low rather. So, that head dissipation is not that fast. So, temperature inside a particle Ti is greater than the temperature outside particle, right.

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Now, the rate of the reaction as we normally say rate of the reaction is typically at of course, when the particles are molecule is close the catalytic side. The rate of the reaction is k into CA raise to 1 where I did for a then it would be minus right now this k is A 0 exponential minus E by RT CA raise to n. Now, if you look at this is A or A 0 this is frequency factor right. Now, there are 2 parameters which feeder rate the temperature and concentration normally, in isothermal case temperature is same throughout and same as the external surface.

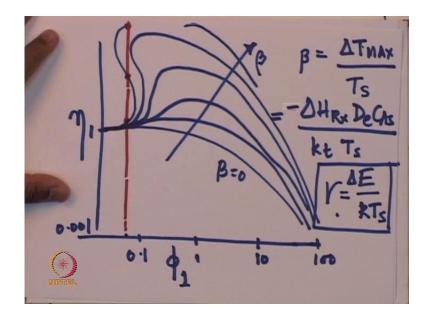
Temperature is only the concentration that changes in normal a situation or whatever we have discuss before this that is for isothermal case. The concentration inside a particle is less then concentration and external surface. So, this reduces the rate inside a particle, but now look at this expression not just CA, but T is also changing now this T inside is greater than the t at the external surface.

So, this 2 parameters CA and temperature they will affect the rate, but relationship are opposite. That is increasing temperature would cause increasing rate right, but there is a

reduction in concentration because of pore diffusion effects; that means reduce the rate. So, now, the overall effect of these 2 changes that is temperature and concentration on the rate is going to decide whether the internal rate or rate inside a particle overall rate average or other integrated overall entire particle. That rate is going to be higher than calculated that at a external surface.

So, there are situations its lightly there are temperature would go up such that it will compensate for the effect of concentration and the rate inside the particle would be greater than that calculated at external surface. In that case is effectiveness factor becomes 1 sorry greater than 1 right.

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So, let us look at relationships. So, let us plot a graph of phi say for a first order reaction phi 1 and eta again. You have 1 here then say point naught naught 1 is again a log log plot 0.1 1, 10 and 100. Now, this is 1 and you know the famous whatever the relationship that we have already looked at is this right. So, initially on other low values of phi it is constant and close to 1 right and then it goes on decreasing; this is what we have seen. And that is for isothermal effect that mean there is no effects.

So, let us define a parameter, lets define a parameter called as beta which is delta T MAX let me tell you the mining of this delta t max divided by Ts. Now, what is delta T MAX? Delta T MAX is a maximum possible temperature raise that can happen inside a particle. And Ts is a external surface temperature. Now, this particular delta T MAX can be calculated based on heat generated. So, heat generated heat of reaction.

So, delta HR of the reaction right this is a heat generated into De CAS divided by kt again I will tell you the mining of each and every term is a heat of reaction. You know this is diffusivity, this is external surface concentration and this is thermal conductivity; this is thermal conductivity. Look at units this is a dimensionless number. Dimensionless number and this tells you ... So, the numerator tells you about heat generated some proportional to heat generated, maximum out of heat generated is a exothermic reaction will see what will happened in the case of endothermic reaction later. Right now is raise in temperature.

So, and the raise will depend on the thermal conductivity the gradient. So, this particular thing is the delta max and this is delta Ts right. So, for this particular case beta is 0 because we are saying that is no heat effect, we are saying that is no heat effect right. So, what are we seen. So, far is. So, far beta equal to 0. Now this another parameter that needs to be define, of course we can look at elaborate derivation of all this.

But, not going to spend much time here this is for your information, but if you are interesting you can write energy balance also inside particle like what we have done in the case of the component balance, we write energy balance also. So, now, you have 2 equations component balance energy balance play with those equation, solve those equations and you will get a value of eta.

Now, again that is to b done numerically because now we do not have a sate forward relationship for eta, like what we had before. What was it eta is equal to t divided by phi 1 square in the in the bracket phi 1 cottage phi minus 1 phi 1 rather if phi why phi 1 because it is a first order reaction. So, we have a derive a relationship of a first order reaction spherical particle, but then that was for isothermal case. Now, from non

isothermal case will have energy balance also coming into picture and then the solution becomes slightly complicated getting a analytical expression become different.

But you can do it numerically; so you can do it numerically. Now, this is for beta equal to 0 right, now if I increase a value of beta will start seeing trained like this slightly higher value of beta, then this, then this. And of course, you can further do this. What is happening here? So, value of beta is increasing now in order to do these calculations I will have define some other constants also and this another number called as gamma which is nothing, but E by RTs or delta E by RTs. Now, what is delta E is a activation energy.

So, it tells you about sensitivity of your reaction rate constant or reaction rate intrinsic reaction rate towards a temperature that is also important right. Because, if the reaction is not sensitive to temperature at all then there is a problem then even if temperature rises inside a particle it does not have any impact on the rate. Since, as good as no heat librated as for as reaction is concern, because reaction is not going to effected by the temperature raise. So, the effect of temperature raise is who decides that exact it is a activation energy. So, we need to define that activation energy. So, this an another parameter.

So, what the graph that I have made here for different values of beta it is at a particular value of gamma. So, this graph is at certain value of gamma. So, right at for certain gas by gamma I go increasing beta value one of these can change. So, that I get different value of beta right. So, in general beta represents a maximum temperature raise and that depends on many factors and the most important 1 is the heat of reaction and of course, thermal conductivity. As I said like if thermal conductivity is small dissipation rate would not be large and that is why the temperature raise will be large.

So, that is why kt appearance the denominator look at all this. So, you should try and read these equations. So, try and interpret them try and see the effect of different variable parameters right. So, beta shows the effect of heat over reaction. So, it is very pricklier trained that you are seen. So, as value of beta increases as the maximum temperature rise increases as the internal rate increases compare to that of the external rate or rate at calculated the external conditions.

Then the value of eta increases this is 1 and now you can see the all values here greater than 1. And that happen when the heat effects are significant at large values of beta you will get a similar such graph for different values of gamma. So, there are different parameters which would affect the value of eta and from non isothermal case. We have 2 independent parameter is defined as it beta and gamma. So, eta can be greater than 1.

Now, the here I can see a very unusual trade unusual sense like because in imagine what will happen if you have a value of phi say point naught or whatever let me use another colour. What I am seeing here? I am seeing that there is possibility for the given value of phi there is a possibility that you have. 1 value of eta here 1 here and 1 here what is it mean this, this is a solution that is obtained by solving steady state equations for material or component balance and energy balance.

So, I am solving these equations together and I am getting the value of eta for different values of phi. So, suppose a value of beta is very large then I am seeing this I am seeing this trade I have got this trade where you have typical s type curve here s type curve here. Now, this s type curves curve rather gives rise to 3 different solutions that is same value of phi. How do I interpret this how do interpret this can I have 3 different values other under otherwise similar conditions at steady state? Yes, it is possible; that means, I have got something called as multiple steady states here right.

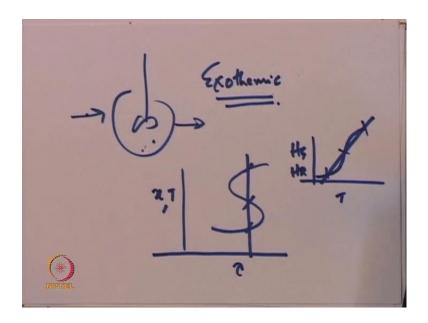
So, for a given value of phi I can realize 3 different possible rates why rates because rate is ultimately eta into k CA. I have 3 different values of eta means I have 3 different values of rates the steady state rate is possible. So, if I am doing the reaction in A CA s t T or the plug flow reactor or any any reactor for that matter. If I am dealing with a solid catalyst reactions solid is porous in nature reaction order can be first order or it can be any other order right and the reaction is exothermic there are heat effects and temperature raise inside a particle significant.

The thermal conductivity is small heat dissipation is relatively less under these conditions for certain values of beta. What I am going to realize is that, there are 3 different steady states possible. Now, multiple steady states is something that you have already learned in reaction engineering part 1 for non isothermal reactors especially, the exothermic

reactors. So, this phenomenon is quite similar to what you have already learnt in the case of exothermic.

Or adiabatic Cstr's exothermic reaction is with adiabatic Cstr's where temperature raise gives positive feedback and your rate also increases you have run away type behaviour and there is a possibility of realising multiple steady states. I hope you remember that hey like what you have learn in the first part dealing with exothermic reactions.

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You have a Cstr exothermic case, I will just quickly revise this non isothermal temperature here is different from temperature here and you have this S type curve you have is convergent and or temperature. And you have some tau here and you see different states possible we have heat generated, heat removed temperature.

This is very quick you have to just go back and look at what you learn before. So, that 3 different steady state possible heat generated curve, intersects the heat removed line for temperature of the reactor this is what we have already learnt. So, why I am referring to this is because this phenomenon that you are seeing in inter particle diffusion its quits similar to what you see the normal exothermic reaction.

So, here also the effect is because of the or this happened because of the heat effects exothermic reaction. Similar thing is happening in the case of reaction catalyst by solving where the heat is significant and temperature rises there and because of that rate constant is increasing in the rate of the reaction is increasing right and I realize multiple steady state.

Now, of course, it is shown graph of phi 1 versus eta where as I use different state variables for Cstr tau verses x and t, but reason is similar. So, whatever you have learned there is applicable to non isothermal reaction with inter particle diffusion as well. We are not going to spend much time analyzing the equations and why you getting steady state and all, because is quite similar what we have learn before.

Another important thing is in these type of curves this is s curve that you have seen this happens that only large only the beta for all value see. Look at relatively small value of beta you do not see multiple steady state only at very large values. Now, these 2 are normally stable steady states and this is unstable steady states this comes. Again quite similar to Cstr steady multiple steady state problem. Unstable means you cannot realize it because it is difficult to have open loop you can have a steady state being stable there.

Though mathematically have a solution stability point of view it is not a stable solution this is something that you learn control theory as well there are stable solution unstable solutions. So, in reality if you want operate a particular say reactor or system it normally gets stable at a stable solutions, but unstable solution you have a proper control to get to that similar unstable solution because system has tendency has go away from it. And probably you learnt all these things in c s t r exothermic reactions.

So, just remember this again you have this curve unstable solution and this are 2 stable solutions. So, it is quite possible that for a given value of phi you have 1 solution for eta which is close to 1; that means, there is no effect of particle diffusion, but it is quite possible that you may get very large value of eta and the rate of reaction would go up right. And that depends on the dynamics of the system how you start your reactor what is a initial condition are they any fluctuation.

So, that you go from us it is state to another steady state; this another practical constraint in this, if you have very large value of eta the internal temperature will go up like anything. These are all theoretical calculations considering that high temperatures are not affecting the catalyst. But, there is a way some practical limit on the temperature at which the catalyst can operate actively can work actively.

Because at high temperature you learn in deactivation that at high temperature the small metallic particle have tendency to come together and they will agglomerate and the surface area of the metal expose to the reaction environmental will go down. And activity will go down is called as sintering. So, every recatalyst has upper temperature limit. Now, what you showing here is not considering all those practical limit assuming that is a catalyst active at any temperature and calculating this eta.

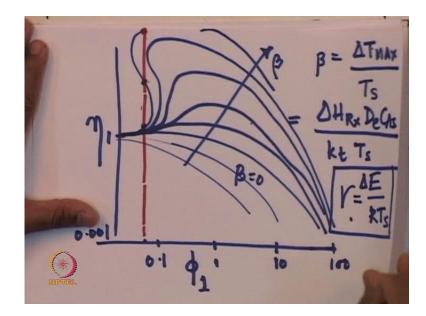
But, then what happens in high temperature catalyst start deactivating the rate constant will go I will change. So, the equation is no longer valid or the value of rate constant we are using is no longer value. So, all this effects are there keep that in mind. So, you may not realize that steady state at high temperature or a high value high value of eta. You may not realize you realize you may not be realize, but if you realize you know the mining of it all right.

So, this is about when the reaction takes place in solid catalyst exothermic reaction and temperature effects are significant. So, I thing this discussion is good enough as for as knowing what will happen if you have exothermic reaction, but then sorry 1 more point if your endothermic reaction will you realise multiple series test do you do you see multiple series there the endothermic c s t r you do not see that why because endothermic reaction effect is exactly opposite I am talking about adiabatic case of there is a lot of heat lost to the surrounding in both the cases in c s t r also and in the case of particle also of course, some amount of heat is lost till you see multiple steady states, but that typical effect of reaction heat is to be is should be evident.

So, now, for exothermic reaction is a rising temperature rising temperature would cause rising rate. So, this is a positive feedback given rising rate would cause increase extend of reaction increase heat and this is the v shape cycle till the reaction is stop, but then this

positive feedback gives rise to multiple steady state is a qualitative explanation is. So, much that 1 1 can this already the so much theoretical development in this area, but let us not get into details of that. But what is necessary this positive feedback will you see the positive feedback in the case of exothermic reaction no because as the extend of reaction is increases the temperature would go down. And that will cause a drop in rate of reaction and that will not give the positive feedback and this renovates that behaviour. So, endothermic reaction you will get only 1 stable steady state. So, in this plot for value of beta greater than 0, go in this direction and less than 0.

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That is when you endothermic reaction you will go in this direction right. So, there is no possibility of multiple steady states in this zone you see the steady only here right less than 0. Means there is a drop in temperature this is not raise delta T is negative we talk about magnitude here delta H is magnitude of reaction, but then for endothermic reaction it will be negative because delta. Delta T that is the temperature delta t max is going to be negative all right.

So, that is how we look at it endothermic reactions will not give raise to multiple steady state will not gives raise to eta greater than 1 eta greater than 1. Only for exothermic reaction is 1 more possibility you can imagine the situation normally does not happened.

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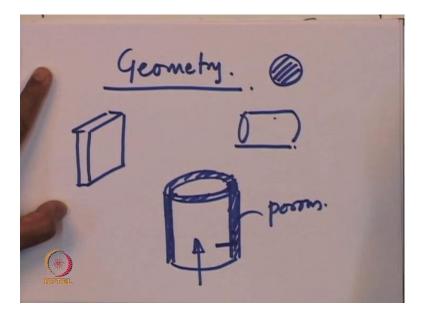
But, then there is a possibility that eta can be greater than 1 for negative order reactions right see like this know for even if it is isothermal. This is isothermal your concentration goes down inside a particle concentration going down is not good for making any of the reaction because rate of the reaction goes down. But for reaction with negative order reaction see r is equal to minus k c a raise to minus 1 or divided 1 1 upon c rather. In that case the dropping concentration gives raise to increasing rate.

So, the rate inside going to go up or is going be higher than that calculated at a external surface. So, there is a possibility either eta can be greater than 1 unusual case is normally we do not come across such situations, but you can imagine such scenarios where there is a possibility of eta being greater than 1. But in reality for exothermic reaction people have observed specially say ammonia synthesis or ethanol synthesis you get.

You dealing with exothermic reactions porous catalyst you see all this effects that is eta can be greater than 1, but not for negative order or not for there. Not for there not many

cases where we come across negative order reaction, but theoretically it is possible to get eta value greater than 1. If reaction is negative order with respective reactant all right. So, we have looked at heat effects. Now, there are certain things that we are not or again we have just made a passing remark while we discuss various aspects 1 thing is about geometry.

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So, far we looked at spherical particles, but there is possibility that you may come across cylindrical particle, because pellets can be cylindrical as well. Or you may have slam possible know is going on you may have a mono see this is your reactor tube. And here coating a tube with catalyst the walls are coated by the catalytic material which is porous natures what is porous. The catalyst porous wall is not porous catalyst is porous and then you reaction reactants are flowing this way.

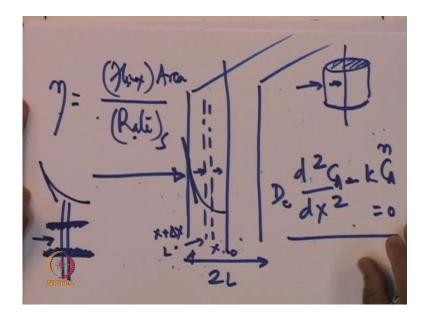
On the way they will get defuse through this and the reaction will take place than many possible scenarios. And everywhere we need to consider the pore diffusion effects as long as you using the pores catalyst. Now, what is the difference between what we have learned here and these geometries? The only difference is the derivation and expression for effectiveness factor and Thiele modulus. I have already told you this there are steps

that we can follow 1 2 3 4 to get the expression for effectiveness factor or Thiele modulus.

What are these steps you have to write component material balance use proper boundary conditions a differential equation with boundary conditions gives you the concentration profile inside a pellet, let it be spherical cylindrical slab. Whatever and this concentration profile helps you get the rate at the external surface. And rate inside a particle concentration profile gives a rate inside a particle external surface you know like R is equal to k CA s raise to n whatever right.

So, effectiveness factor is a rate calculated based on the flux divided by the rate at external surface. So, this numerator that is a rate calculated in the flux will be obtained by the concentration profile and this concentration profile comes by writing the component balance for different geometry. We already done it for spherical particles right you can do it for say slab example I want to derive this.

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But I can imagine slab with thickness say l. Or 2 l there is a symmetry here of course, a slab is like this. But that is insulated from all the sides only the diffusion taking place in this direction right then I can consider a differential element here like what I did for

spherical particle and then this is my x. So, this is 0 and this is 1 this is x and this is x plus d x right i can write balance for this differential element. I get differential equation which will be on the form say d to c by d x square d e something like this, minus what k rate constant in proper units into depending on their order of reaction k CA raise to n is equal to 0.

Something similar and then I write boundary conditions again at x is equal to 0 you have the flux 0 on concentration of finite. And you know the external conditions use those boundary condition you have a set of equations. So, solve them either the analytically or numerically and you get a concentration profile. You get a concentration profile how do you calculate eta you have flux into area divided by rate at the external surface. This is quite state forward area you know this into whatever be flux comes from the concentration profile it is this gradient.

D c by d x or in dimensionless form it is d psi by d lambda all ready I have got a concentration profile get a gradient put it here and you get a value of eta. So, that is a general procedure. So, I have just shown you what happens in the case of slab similar thing for cylinder use cylindrical coordinates. Here, you assuming that this is all non catalytic diffusion is taking place on the like this you can write this for any geometry.

Where the pore diffusion is significant people have done it for a pore like it is cylinder through which there is a moment a particle sorry not particle it is a molecules. This is a diffusion taking place and this is very small pore, but then there is a catalyst on the wall. Something similar to I have what I have shown just now where you have catalyst coated on the wall of the reactor.

Now, consider this as a reactor this small pore, but consider this is tiny reactor where you have the diffusion taking place no convention diffusion taking place. I can write similar equations differential balance in out get a profile get a profile get a gradient put it here and you get a value of eta. So, so do not get confused if you have different geometry the remember the procedure right that is more important concept is important. So, for a 3 different geometries the first 1 of course, is spherical you have the values of phi first sphere file is equal to R root of k 1 row.

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C s a divided by d e for first order reaction the moment that write in k 1 it is first order reaction, then for cylinder if you follow same procedure what you will realize is phi is equal to r by 2 now. So, it that 2 comes out of that what surface area volume and all relationship with radius here came appropriately because, 4 third phi r cube right 3 came there. So, this is cylinder first order slab 1 now, there is no R for this slab k 1 s a row c divided by all in the square root.

So, look at this factor in the square root it is same throughout it is an change nothing do the geometry only the part here is different from geometry to geometry. And once you have that then the relationship of phi with respective eta will be similar for the sphere cylinder and slab. So, respective of any geometry relationship between the similar; that means, as phi increases eta would go down.

So, only the value of phi and would matter for the geometry once you get phi then you have the concentration profile in the form of phi typical relationship. And this relationship will not change from geometry to geometry for every geometry you will have the same relationship between eta and phi which is 3 by phi whatever cottage phi into phi minus 1.

Similar of course, now let us look at some possible examples in the case of like we not at solve any solve any problem there is many problem there is many text books Foglers books. There many interesting problem you can try and solve them the solutions are also given this 1. 1 of these problem will have look at it again will not going to solve it completely. But, I will tell you how to solve.

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So, there is 1 problem in Foglers book which is again for a simple reaction a going to b the first order reaction reverse irreversible spherical particle right. Now of course, you have platinum coated on some support particle or pellet whatever you say it can. If you it is small then is called as particle and if it is especially made to through the requirement or rather to meet the requirement of what you need in fix bed reactor. It is pellet right fine what they have given you is the reactant concentration the reactant concentration CA right. Half way between external surface and the centre or the pellet is equal to 1 tenth of CA as that is external surface concentration right.

So, you have CA by CAS is equal to point 1. So, c a by CAS is equal to point 1 the concentration at external surface c a as is equal to point naught naught 1 gram moles per d m cube. The diameter of the particle is 2 into 10 raise to minus 3 c m that is centimeters with the a diameter of the particle is all is given the diffusion coefficient effective

diffusion coefficient is point 1 centimeters square per second. See the value order of magnitude, which not yet look at these values numerical values. So, fields for this numbers.

This is a data given to you right and from this data what is asked is now what. So, this is your spherical particle this is a centre you know the concentration half way through you have been given this data. And what is asked is the concentration of the reactant at a distance 3 into 10 raise to minus 4 centimeters from the external surface 3 into 10 raise to minus 4 centimeters from the external surface 3 into 10 raise to minus 4 centimeters from the external surface 3 into 10 raise to minus 4 centimeters from the external surface. The data given is half way through that is if the particle diameter is 2 into 10 raise to minus 3 the radius is 1 into 10 raise to minus 3 half way through is point 5 into 10 raise to minus 3.

So, this distance is point 5 into 10 raise to minus 3 now I am looking at what I want to calculate is the concentration at a distance 3 into 10 raise to minus 4 centimeters. It is very simple problem what will you do you know the equation for the concentration profile.

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$$\begin{aligned} y &= \frac{C_{A}}{C_{A}} = \frac{1}{\lambda} \frac{\sinh \phi}{\sinh \phi} \\ \psi &= \frac{C_{A}}{C_{A}} = \frac{1}{\lambda} \frac{\sinh \phi}{\sinh \phi} \\ 0.1 &= \frac{1}{0.5} \frac{\sinh (\phi x 0.5)}{\sinh \phi} \\ \psi &= 6 \end{aligned}$$

What is it; CA divided by CA as psi is equal to 1 by lambda sin h psi into lambda divided by sin h what is it sin h phi, psi. This phi phi this is phi that is a Thiele modulus. So, this

equation is given to you or is known to you rather right. So, from this equation you know is given 0.1 for lambda 0.5 sin H lambda point phi divided by sin h phi. So, you have this equation only phi is unknown you can use try and error to get a value of phi which will be close to say 6 here right. So, once you know the value of phi again what is asked is what the concentration at a given radius is.

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$$\Psi = \frac{C_{A}}{C_{AS}} = \frac{C_{A}}{0.001} = \frac{1}{7} \frac{\sinh(6\pi)}{\sinh(6)}$$

$$\lambda = \frac{\Gamma}{R} = \frac{R - 3 \times 10^{11}}{R} = \frac{1 \times 10^{3} - 3 \times 10^{11}}{1 \times 10^{3}}.$$

$$Q_{A} = 2.36 \times 10^{9} \frac{\text{mols}}{\text{Jm}^{2}}. = 0.7.$$

So, again psi is equal to Ca divided by Ca is equal to divided by what is it point 1 it is the concentration at external surfaces is point naught naught 1 point naught naught. 1 is equal to 1 by lambda sin h say phi which is 6 into lambda divided by sin H 6. So, what is lambda 3 into 10 raise to minus 4 from the external surface. So, lambda is equal to r by R external surface; that means, r minus 3 into 10 raise to minus 4 divided by R. What is r? R is 1 into 10 raise to minus 3. So, 1 into 10 raise to minus 3 into 10 raise to minus 4 divided by 1 into 10 raise to minus 3. So, this becomes 0. 7. So, substitute 0.7 here get a value of c a. So, after substituting the CA is about 2.36 into 10 raise to minus 4 moles per dm cube I will complete this solution in the next class.

Thank you.