

Chemical Reaction Engineering II
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Lecture - 11

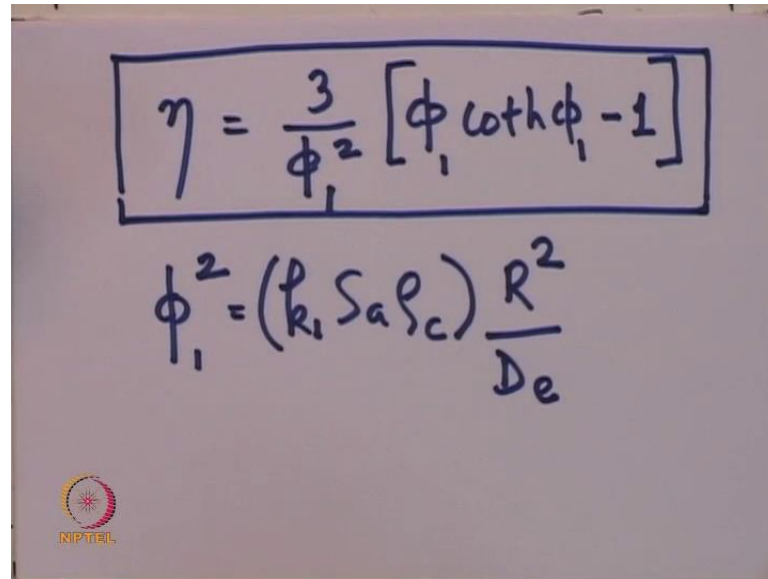
Intra-particle diffusion Thiele modulus and effectiveness factor Part – II

So good morning. Let us continue our discussion on effectiveness factor in the last lecture, we looked at how to get a concentration profile based on a boundary conditions that we have. And then the concentration profile which was derived for first order reaction intrinsically first order reaction that was used further to get the expression for the effectiveness factor.

Now, I told you effectiveness factor is a factor that normally lies between 0 and 1 for isothermal reactions. Non isothermal, it can go beyond 1, we will look at it separately. But, then it tells you how important is the pore diffusion, there was 1 more factor that, we defined earlier that, was Thiele modulus. Now Thiele modulus can take a value from 0 to infinity k it does not have any limits as such.

So, but then very large Thiele modulus means; more pore diffusion resistance and we need to consider the pore diffusion effects while deriving the looking at the rate of reactions and small value of Thiele modulus is where pore diffusion resistance is negligible. So, there is a inverse relationship between Thiele modulus and effectiveness factor fine.

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$$\eta = \frac{3}{\phi_1^2} [\phi_1 \coth \phi_1 - 1]$$
$$\phi_1^2 = (k_1 S_a \rho_c) \frac{R^2}{D_e}$$

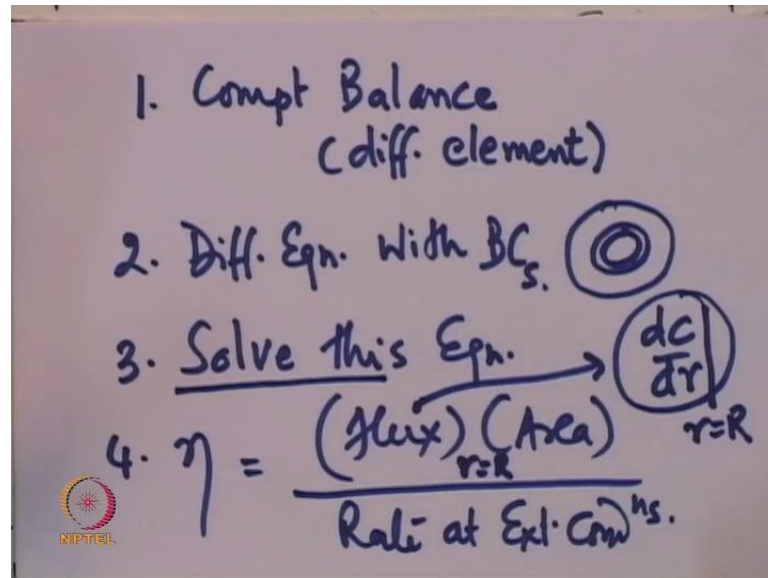
So, let us look at a effectiveness factor equation or expression that we derived in the last lecture ok eta is equal to 3 divided by phi 1 square why 1, because we are talking about a first order reaction now into phi 1 cot h phi 1 minus 1. And you know what phi is; phi is the Thiele modulus for the first order reaction which is nothing but or let me call this is phi 1 square which is nothing but $k_1 s_a \rho_c$ you know what all this is. This is reaction rate constant per unit volume of the catalyst pellet or particle into r square divided by d_e .

So, I have this relationship which tells me, how the effectiveness factor varies with respect to phi that is Thiele modulus. Now I can plot this relationship and see how it looks. So, for the first order reaction and its spherical particle remember. We have bring all the exercises for a spherical particle. We assuming particle to be exact sphere, but it may go away from the sphericity and you have it may go away from the spherical shape I we need to incorporate those effects also shape factors .You may have cylindrical pellet, you may have a slab.

So, the shape also matters because all the equations that we are derived of all spherical particle. So, the effectiveness factor that, we have derived is applicable to spheres and for the first order reaction very important just remember, what we have done all right. So, before we go ahead. Let me quickly revise, what we have learnt because this procedure that we have followed is very important that can be used for deriving or getting the rate getting the expression for the effectiveness factor for other geometries.

As I said you may have a cylindrical pellet, you may have some other geometry say slab. So, in those cases how to get a effectiveness factor. We have to follow certain procedure. So, what have you have it done here, same procedure as to be followed, but of course, applicable to that particular geometry.

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Now, what we have done is we have taken a balance ok. Component balance which is the form of a differential equation, component balance it differential element, in the geometry remember for sphere it was a differential element right once we have that. So, you get a differential equation, with appropriate boundary conditions try and solve this if possible why we want to do that, because effectiveness factor is equal to flux into area external area divided by the rate at external conditions right.

This flux is nothing but of course, this is proportional to $d c$ by $d r$ or x whatever, is a gradient of course, just we multiplied by diffusivity with their appropriate sign and so on. But, the gradient is important and if you want to get a gradient at r is equal to r or at the boundary flux at r is equal to capital r for a spherical particle, but in the case of a slab it would at x is equal to l right. So, at the external surface where, I am sitting and observing the molecules going inside a pellet, inside a particle and at the rate at which they are going inside.

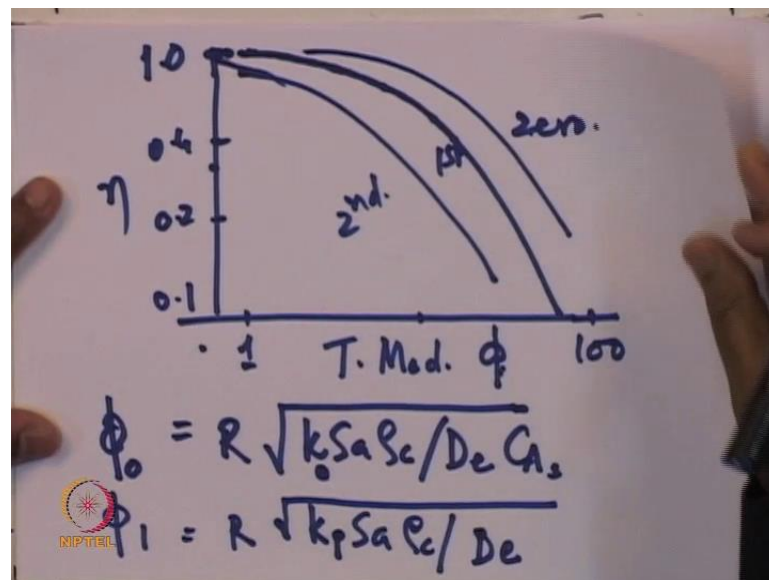
So, flux into area flux is always per unit area all right. So, look at this equation and need this and that is the reason I am getting the I am solving the equation to get a

concentration profile then substitute it here and whatever you get is the expression for the effectiveness factor for simple cases like spherical geometry and first order reaction it is easy to get analytical solution on a expression for effectiveness factor.

For nth order reaction or for some complex geometry it will not be possible to get a expression for the effectiveness factor as such, it will be a quite complicated you will have set of equations to be solve simultaneously, get a value of eta that is effectiveness factor. So, this is the general procedure how to get eta, we may if time permits probably we will look at different geometries or 1 more geometry to get a value of effectiveness factor flowing this particular procedure.

So, that it will be clear and of course, while writing these equations the coordinates are very different right now, we is in spherical coordinates. But, in the case of slab it will be what it will be a long length. Cartesian coordinates in the case of cylinder it will be cylindrical coordinates all right. So, the procedure remains same, but then of course, we have to taken to consideration the geometry, fine.

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Now let us look at a relationship how it looks phi versus eta. I am plotting a log-log plot. So, I have this Thiele modulus value varies from say here, you have 1 then you have 10 somewhere and then you have 100 somewhere. It is a log-log plot it is a log and again here you have say 0.1 effectiveness factor 0.2 0.4 and so on, finally, it will be 1 here ar.

Now, it is easy the relationship is inverse it is going to go like this. Now, at very low values of ϕ let us, talk about the first order reaction that we have derived expression for at very low values of Thiele modulus the value of effectiveness factor is going to be 1. So, 1 here right maximum value for isothermal reactions and it will remain 1 over a range for very small values ϕ depending on what is a rate constant so, many other factors how these 2 things play with each other. There is a inter play of reaction and diffusion.

Now, as we go on increasing the value of ϕ effectiveness factor is going to go down and this is what your likely to see the relationship between η and ϕ remember now, we go to now, going to 0 its point 1 is a log-log plot we have. So, it is very clear that as ϕ increases the effectiveness factor goes down. And what is effectiveness factor effectiveness factor tells you what a resistance of pore diffusion is. So, if the pores are open then my rate of reaction is r is equal to $kC_a S$ that is surface concentration raised to n , but at CAs is not seen by all the catalytic sides.

If there is pore resistance, because inside a catalyst particle the concentration drops down right and that is the reason the reaction rate drops down, if you have pore diffusion resistance. And that is why the effectiveness factor goes down and I get a value say 0.1, 0.2, 0.4 whatever, if it is 1 then you are comfortable; that means, no pore resistance. Now, this is for a first order reaction; for a 0 order reaction, it would be somewhat like this what effectiveness factor will be more for the 0 order reaction compared to first order reaction for the same value of Thiele modulus probably.

Because, the sensitivity towards the concentration is relatively less, it is a concentration that matters right because concentration goes down inside a particle right. Sensitivity is less than and that is why the effectiveness factor is slightly higher. For the second order reaction it is sorry it should any way start from 1 it is this way. So, this is for the second order this is for the first order and this is for the 0 order, we have derived equations for ϕ remember we have derived equation for ϕ for 0 order first order second order any order n 'th order ϕ n .

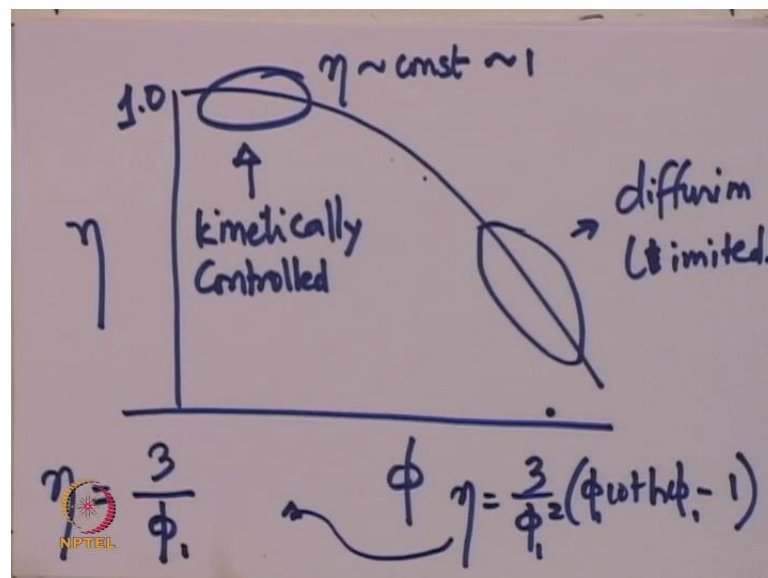
So, this ϕ is for 0 order first order second order. So, let me write ϕ is 0 is equal to r into $k_s a \rho C_a S$ right CAs is coming down here, why because its CAs to n minus 1 inside a root. So, n minus 1 is 0. So, its minus 1 CAs is coming down right. First order

η is equal to r , this is what we have already derived $k_0 c_0$. Let me write k_0 because it is rate constant for 0 order reaction this is $k_1 c_0$ and now $n-1$ $1-1$ 0 .

So, there is no concentration dependency there is no concentration dependency η you can write the expression for η . So, what will be the expression for η η is if you make η here then instead of k_1 I have k_2 here and we have to multiply it now, by C_A because now its $n-1$ that is $2-1$ c_A will appear in the numerator. So, η varies if the order of reaction varies we have already seen that right. So, this is the relationship for every, for different order relationship will also change.

The equation that we derived that is $\eta = \frac{3}{\phi} \left(\frac{\phi}{2} + \sqrt{\left(\frac{\phi}{2}\right)^2 + 1} \right)^{-1}$ what was that relationship, for it was for the first order reaction do not get confused that is not a general relationship. For second order relationship will be will be different, we do not have expression for that, but I can always calculate by iterations by solving those equations simultaneously and get this plot get these plots; for first order anyway we have the expression all right. This is how it looks.

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Now you have a general plot, showing the relationship between ϕ and η ; I am not again going to show the coordinates and all. Now, that 2 distinct regions in here, the 2 distinct regions here. So, this is 1 region here and where η is almost constant. Now, this is the region where reaction is not a effective by pore diffusion this is kinetically

controlled, pore diffusion effects are insignificant, η is almost 1 constant means 1. Now, there is another region, where η is changing drastically with ϕ what is happening here.

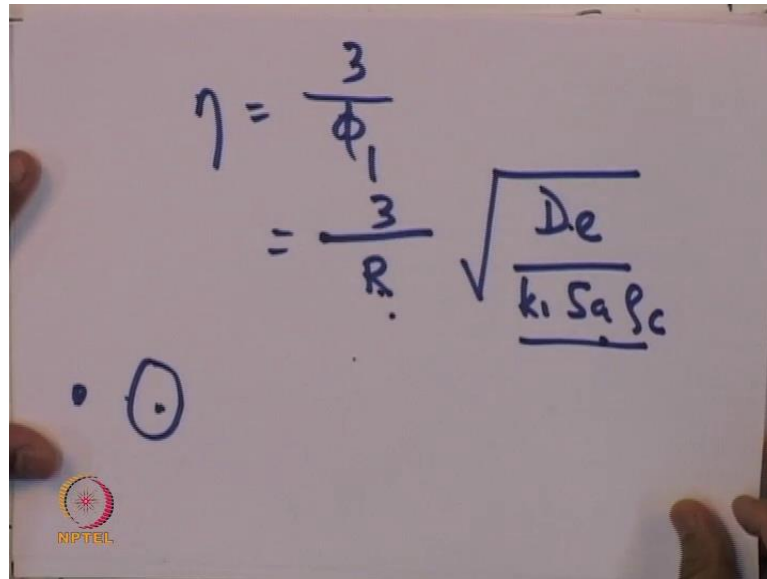
Because value of ϕ is increasing the pore resistance is increasing and η is going down; that means, the effectiveness factor is going down resistance is much larger now here, the control is taken over by the diffusion and not the reaction. So, in this part, it is the diffusion control or diffusion limited sorry diffusion limited. It is very important since we are in this region then there is no point in working on both parameters, which increase a intrinsic reaction like for example, temperature will have, will not have that impact on the rate if you have here.

It will have some impact we are going to see that but it will not have much impact on the rate compare to what it would be when you are here right other way around suppose, you are here then do not work on reducing the effect of diffusion why, because diffusion is always already its friendly its cooperating; that means, there is now issue here as for as diffusion is concern. So, do not try to increase the pore volume do not try to increase the effective sorry effective diffusivity do not try reduce the particle size, very important particle size I will talk more about it bit later.

So, here in this region where reaction is controlling or when it is kinetically controlled, then try and increase the temperature increase the temperature you are rate will increase drastically are nous equation or law right. So, this plot tells us a lot diffusion control, reaction control what about this region both of them are important right both of them are important. Now, in this particular region now you are relationship gets a bit simplified. If it is a first order reaction, what we had looked at was η is equal to 3 divided by ϕ $1 - \cot h \phi$ minus ϕ $1 - \phi$ this was a relationship that we derived.

Now, what happens is that if ϕ is very large η becomes equal to 3 divided by ϕ η becomes equal to 3 divided by ϕ it becomes very simple if its ϕ 1 , of course become a very simple relationship.

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The image shows a handwritten equation on a whiteboard. The equation is:
$$\eta = \frac{3}{\phi_1} = \frac{3}{R} \sqrt{\frac{D_e}{k_1 S_a \rho_c}}$$
 Below the equation, there is a small diagram of a circle with a dot in the center, representing a particle. In the bottom left corner, there is a logo for NIPTEL.

Now, where as substitute for phi, phi 1 rather eta is equal to 3 divided by phi 1 is equal to 3 divided by r root of $D_e / k_1 S_a \rho_c$, I am substituting for phi 1 for first order reaction. So, look at this eta effectiveness factor keep this in mind, I am not saying you should bhayat it and always like sometimes you know you can interpret the things based on the equations or if you remember those equations they help you sometimes to come with the quick estimate or interpretation of what is happening fine. And in this particular case eta is larger for smaller radius or is for a smaller particle.

Now, you have 2 particles who will offer more resistance, this particle will offer more resistance why, because the molecules have to travel a longer path; to reach all the sides from this to this where as the sides inside the small particles are accessible better then what would be here because there is not much distance to be travel. So, that is the significant of this like, if your particle is smaller the value of eta is large pore resistance goes down overall pore resistance. D_e effective diffusivity its quite obvious if the effective diffusivity is very large value of eta is very large simple and look at the denominator it is a rate constant.

So, the intrinsic reaction. Intrinsic reaction that means; when the molecule is seeing the catalytic side: intrinsic reaction adsorption, surface reaction, and dissadsorption 3 steps remember. So, the combined equation that we get for this when a molecular is near the catalytic surface from that I am getting this intrinsic rate if you neglect dissadsorption

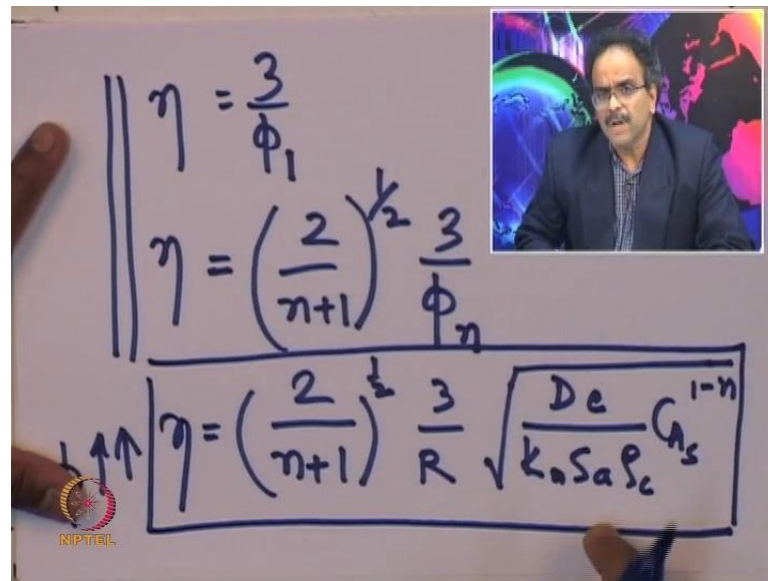
and adsorption then it becomes surface reaction and this is the k_1 is the reaction rate constant that we are talking about. So, this intrinsic rate constant also important say if the reaction is intrinsically very slow what will happen? η will become very large why because reaction is slow and diffusion becomes relatively fast.

So, diffusion does not have impact on the reaction if intrinsic reaction that is the value of $k_1 a \rho_c$ is very large is instantaneous, in that case your problem in the sense the pore resistance will play an important role, because reaction is become very fast. So, all these individual factors are D_e and intrinsic reaction rate constant together all these together; these 3 factors are very important as far as effectiveness of a particle catalytic particle are concerned. So, there is better to keep this relationship in or equation in mind though this is applicable to first order reaction.

For any n th order reaction you know there will be some other terms related to surface concentration as well for first order reaction that is the only order or reaction in which effectiveness factor is not. A function of concentration surface concentration both effectiveness factor and a Thiele modulus. So, this is a significance of effectiveness factor and for very large values of ϕ it becomes simple relationship η is equal to $3/\phi$.

Now, what happens if you have n th order reaction a general n th order reaction if diffusion effects are significant again you can derive the equations, it will be slightly complicated and then if you make simplification saying that value of ϕ is very large, what is it mean; value of ϕ is very large means diffusion effects are significant, if you see that particular plot and towards zone where inter particle diffusion controls the overall rate in that case they have come up with the rate they have come with a expression straightforward expression for effectiveness factor which is given by.

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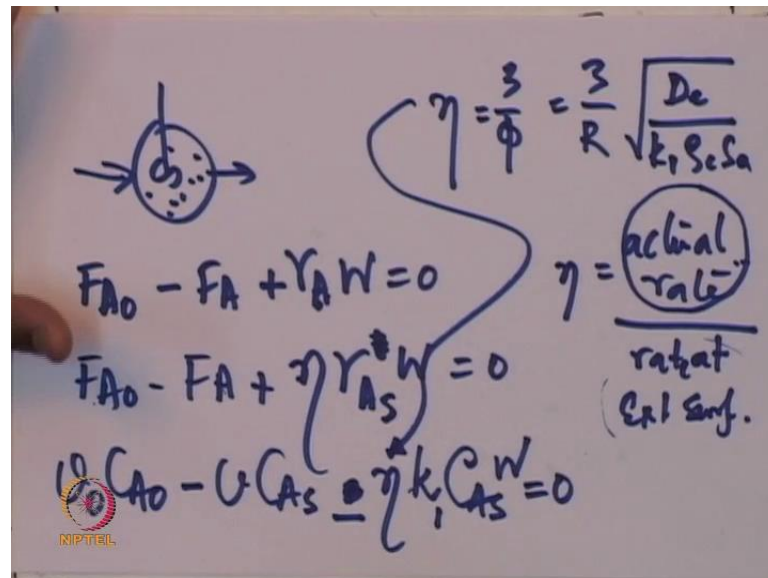


The image shows a whiteboard with handwritten equations. At the top left, $\eta = \frac{3}{\phi_1}$. Below it, $\eta = \left(\frac{2}{n+1}\right)^{\frac{1}{2}} \frac{3}{\phi_n}$. A box contains the equation $\eta = \left(\frac{2}{n+1}\right)^{\frac{1}{2}} \frac{3}{R} \sqrt{\frac{D_e C_{A_s}^{1-n}}{k_o S_a \rho_c}}$. An inset video shows a man speaking. A NIPTEL logo is in the bottom left.

Now for first order reaction we already know it is ϕ_1 , but then for n th order reaction it becomes 2 by n plus 1 raised to 1 half that is square root of 2 by n plus 1 divided by into 3 by ϕ_n . So, this is effect this is Thiele modulus for n th order reactions can I expand it further or rather elaborate it further 1 half 3 by r root of $D_e K_a S_a \rho_c$ rho C_{A_s} raised to or C_{A_s} raised to 1 minus n . If it takes this out 1 minus n by 2 if you take C_{A_s} out it will be 1 minus n by 2 .

This is for ϕ very large very important I mean; its whole where particle diffusion is controlling not in the intermediate zone not in the zone where reaction kinetic is controlling the overall rate. It is the diffusion that is controlling the value of ϕ is very large value of η is relatively small. So, this equation is very important I am going to come back to this all right. So, we talked about relationship it will be η and ϕ we have spend some much time understanding this significance of η we spend time in understanding the effect of parameters like: effective diffusivity, radius of the particle and intrinsic rate constant how they impact, how they make an impact on effectiveness factor and so on. Now, what is if objective is to design the reactor remember I have told you in the last lecture also say.

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For example, I have a CSTR, I want to design this CSTR solid catalyze reaction it can be fluidized bed reactor it can be a spinning basket reactor it can be a plug flow reactor whatever. So, I have performance equation say for example, have a CSTR performance equation is $r_A W$ is equal to 0. Now, what is this r_A is a entire exercise here is meant; for getting a right equation for r_A or expression for r_A in a normal case. It is case a if you taken to the adsorption disadsorption and have langmuir, hinshelwood whatever, but then if there is effectiveness factor coming in picture is a pore diffusion that is coming in picture it becomes.

Now, very simple how to consider, the effect of pore diffusion in the design equation all I need to do here is F_A is 0 minus F_A plus eta into r_A intrinsic is equal to 0, what is r_A intrinsic, it is well is no pore diffusion in the resistance remember the denominator term in the expression for effectiveness factor when the pores are opened up all the sides are exposed to the external environment right. So, that is nothing but the rate for calculated at the external surface, but because there is pore diffusion resistance the overall rate or the actual rate will become equal to eta into this remember eta is equal to actual rate divided by rate at sorry rate at external surface.

Now, I am interested in the actual rate right I mean as far as design is concerned I am interested in the actual rate. So, this is actual rate right. So, actual rate is eta into the rate calculated at the external concentration, because here we have external concentrations I

hope it is clear. So, instead of r_{Ai} now, I can say r_{As} why because this is calculated at x external surface and this r_{As} will be in terms of CAs and this CAs is nothing but or FA is nothing but volumetric flow rate into CAs right.

So, I can write this as if it is a first order reaction then $k C_A$ of course, there should be negative sign here because, it is a reactant if it is product to be positive right. So, fine now, I can solve this equation sorry it should be w here I can solve this equation if w is given I can calculate CAs that is convergen if convergen is given or CAs that is outlet concentration is given. I can design the reactor to how much catalyst is required provided I know η provided, I know η and I have told you how to calculate η based on the properties of the catalyst.

For the first order reaction η is: equal to 3 by ϕ if it pore diffusion controls strongly pore diffusion control is equal to 3 by r root of what is it De into k 1 ρ c s a right. So, this will come here for the first order reaction fine. This is how I solved a design problem this is how I deal with a reactor. So, all exercise last 2 lectures that we have spent or 2 or 3 lectures that, we have spent on effectiveness factor from reactor design point of view it is only this factor that is important and it comes from this expression. This is for first order of course, for other orders we will have different equations all right effectiveness factor.

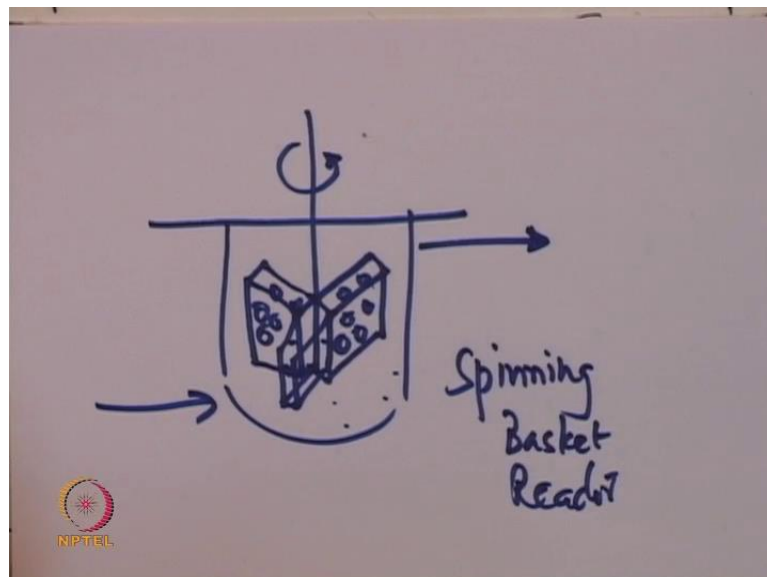
Now, effectiveness factor will change your kinetics and it may give an impression that reaction is behaving very different. Now suppose, you know inter particle diffusion and try generate some data in laboratory, you will get some effects which are probably not excepted for example, say activation energy we need reduce or increase in the presence of pore diffusion resistance. If you have pore higher larger pore diffusion resistance the activation energy is going to go down why, because the sensitivity to the changing temperature of the reaction rate will reduce.

If you have more pore resistance Arrhenius law is applicable to intrinsic chemical reaction and with the pore diffusion. Pore diffusion that sensitivity temperature will relatively less, it is not it does not come in the form of Arrhenius law. So, the there is a problem, then if you have pore diffusion then you'll see the activation energy which is reduced drastically and you would not except that low activation energy. So, such things are possible ordered will change in the sense current order or observed order in the

experimental data will be much different or like to be different rather than the actual order.

So, we are going to see if there are pore diffusion effects what are the observations are possible when I do experiments in laboratory. Now, what kind of experiments I am going to do in laboratory you already seen the different laboratory reactors, a fixed bed reactor a differential reactor they can be possibility of slurry reactor having a slurry reactor, batch reactor, specially for catalytic pellets is something called as spinning basket reactor, which is quite common in laboratory to generate a data for such reactions; what is spinning basket reactor this is the reactor with a normal reactor.

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Let me draw it this way, you have stirrer in a normal reactor. Now this stirrer, will have basket attached it. Now, why basket there will be another basket like this and when I have when I have stirrer this or when I give motion to this shaft this entire basket rotates. So, this basket is attached to the stirrer. Now, what is a purpose of this basket it holds the catalyst it holds, the catalyst these are catalyst pellets.

Now, what is happening here is instead of putting the catalyst pellets outside I am putting them inside a basket why, because it is likely that because of intense agitation these particles pellets made disintegrate or rather get make it converted it to fines small particles and you know the importance of radius here, you know the importance of

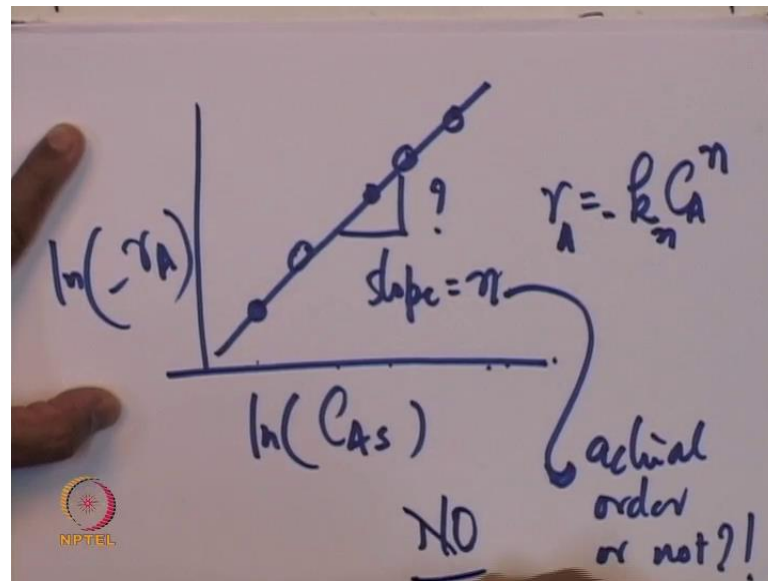
particle size here. If it gets converted to fines then the pore diffusion, if it is important the reaction rate will get will increase because of the particle size is come down.

So, I do not I want to see the real effect what exactly is the pore diffusion effect ,I do not want particles to get converted to small particles because of some mechanical action and I have put them inside a basket. So, remain impact at a same time, I need agitation to overcome the other resistances especially the external mass transfer resistance, we are going to learn the effect of mass transfer resistance later, but then that effect is also nullified or rather it is a reduced here are almost eliminated here by a having very high speed of agitation.

So, this is called a spinning basket reactor, very common that is why I spend some time on this spinning basket reactor. I am doing in laboratory say I am using a spinning basket reactor it is in a CSTR mode say that is reactant going in product coming out and I do some experiments and determining the rate determining the rate and from this rate I back calculate the reaction kinetics, what is it mean in the first part of reaction engineering course for normal homogeneous reactions. You have spent time estimating the kinetic parameters like: rate constants, out of the reactions from the laboratory data right.

So, from the laboratory data how to get a rate constant and all you already know about it the same thing, I am doing here. Now, instead of using a simple reactor there I have a spinning basket reactor, I have told you the purpose of that and from CSTR from inlet outlet concentration, I know what the rate is at; which the reactions taking place or you may use a differential reactor right. And then I calculate rate at different concentrations, I calculate rate at which different concentrations, I we have plot them if I plot them what do I get?

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I get relationship like this: C_{As} that is a external concentration and a rate you can take the modulus of that like, if it is a reactant and then if you minus. So, the quantity would be plus right, if I have these I go on changing the concentrations. And at different concentrations I am calculating the rate or measuring the rate not calculating I am measuring the rate observing certain rate. And I am going to see something like this.

Now, this is a log-log plot sorry I forgot to tell you. This is a log-log plot. So, if I get a straight line what is the slope if I have rate is equal to k minus $k C_A$ raised to n K_n rather a if I take log both sides a of course, negative and make it positive and take log of both the sides then the slope is nothing, but n th order of reactions. Now if pore diffusion is dominating and I generate this data, I am going to get some slope. Now, the question is: whether this n that I am getting is the actual order or not, if pore diffusion effect is not there my early exercise reaction spinning part 1 n is equal to the order of reaction as simple as that.

But, now I am working with pellets I have a spinning basket reactor and it is possible that particle size is large or diffusivity is relatively small. Then that case pore diffusion effects are going to play an important role, in that case the question is whether the n that is the slope that I calculate here is going to be the order of actual order of the reaction or not the answer is no the answer is no why look at this. If you have actual order n , if you

have actual order n then because of pore diffusion effect the order that you see is different from n. So, what is that?

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The whiteboard shows the following derivation:

$$r_{A, \text{obs}} = \eta \cdot r_A$$

$$= \left(\frac{2}{n+1} \right)^{\frac{1}{2}} \frac{3}{R} \sqrt{\frac{D_e}{k_n S_a \rho_c}} C_{A_s}^{\frac{1-n}{2}}$$

Below this, there is a note: $k_n C_{A_s}^n$. An arrow points from this note to the term $C_{A_s}^{\frac{n+1}{2}}$ in the final expression:

$$= \left(\dots \right) C_{A_s}^{\frac{n+1}{2}}$$

A NIPTEL logo is visible in the bottom left corner of the whiteboard image.

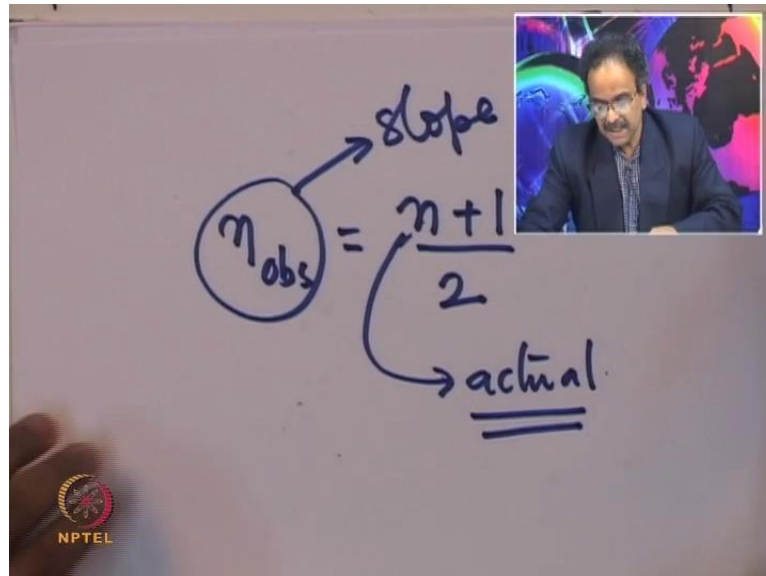
So, the rate is observed is equal to eta into the intrinsic rate right. So, this is equal to pore diffusion effects are significant pore diffusion effects are significant then what is the value of eta; eta is for any nth order you already looked at this CAs, I have taken it out of the square root that is why I divided by 2. Now, look at the order this is eta and then you have Kn see this particular expression is for eta.

So, I am I have written this for eta and then r_A is equal to k_n , whose having negative sign here k_n into C_A raised C_A raised to n right. So, then you have some number here which is function of D_e then $k_n S_a$ or whatever n and then C_A raised to $n+1$ by 2 right. I am just looking at a term that involves C_A , because C_A raised to n into C_A raised to $1 - n$ by 2 together gives you $n+1$ by 2. You can write here, all this with k_n coming in the nominator and so on.

So, what is happening? Now, this particular term or this says that the order that I am not going to see when the pore diffusion effects have significant, when the pore diffusion effect is significant is $n+1$ by 2 whereas, the actual order is n right. So, this is called as falsified kinetics that means; the actual kinetics is different, where in the presence of pore diffusion effects if do a experiments in laboratory try and interpret that data I am

likely to get an order which is different from what it is actually as for as the intrinsic kinetic is concerned.

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$$n_{\text{obs}} = \frac{n+1}{2}$$

Annotations: An arrow points from n_{obs} to the word "slope". Another arrow points from the denominator "2" to the word "actual", which is underlined twice.

So, the apparent order becomes or n_{obs} becomes $n+1$ by 2. So, you are going to get this. So, this is going to be a slope from the experimental data and if I want to calculate actual order it is going to be 2 into an observed minus 1. And this is my actual order actual I hope it is clear how order will change if the pore diffusion effects are significant I am doing experiments in laboratory; what will happen to activation energy, I will come back to this expression.

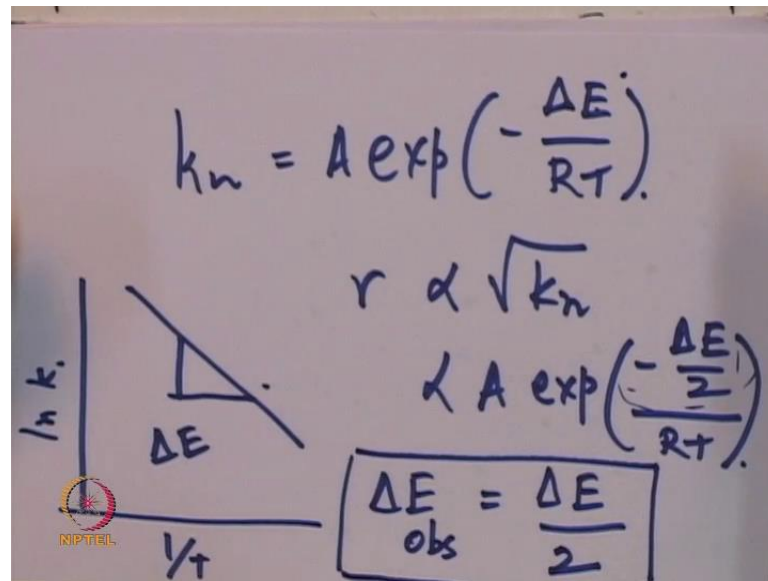
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The image shows a whiteboard with handwritten mathematical equations. At the top, it states $\gamma_{A,obs} = \eta \cdot \gamma_A$. Below this, a more complex expression is written: $= \left(\frac{2}{n+1} \right)^{\frac{1}{2}} \frac{3}{R} \sqrt{\frac{D_c}{k_n S a L_c}} C_{As}^{\frac{1-n}{2}}$. To the right of this expression, there is a note: $k_n C_{As}^n$. Below the main expression, there is another equation: $= \left(\sqrt{k_n} \right) C_{As}^{\frac{n+1}{2}}$. An arrow points from the $\sqrt{k_n}$ term in the second equation back to the k_n term in the first equation. In the bottom left corner of the whiteboard, there is a small logo for NPTEL.

Look at this look at this I have this. Now, where is a activation energy coming in picture; activation energies because of the effect of temperature on K_n right. Now, again there will be some constant but now look at k_n . Now, I will separate the terms of K_n k_l will appear in the nominator like this: $\sqrt{k_n}$. So, even if the reaction is first order, the dependency of rate on K_n is not straightforward see.

If this was not there sorry it was not there you have rate is directly proportionally to K_n whereas, now because of this factor what is happening is rate observed is proportional to $\sqrt{k_n}$ and not only k or not K_n rather its $\sqrt{k_n}$ k_n raised to 1 by 2 right. Now, let us look at the activation energy; what is activation energy Arrhenius law.

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Arrhenius law k_n is equal to is frequency factor exponential minus delta e by RT, how I get activation energy I have told you $\ln k$ versus $1/T$ and slope gives me delta e right. This is how I get it. So, what I am going to do in laboratory, I will do experiments at different temperatures, I will get values of rates. From rates, I will calculate rate constants or initial rates will directly; will give you the rate constant because you know the initial concentrations for batch reactor for continuous reactor. If I know the concentration from concentration, I can calculate a rate constant if the rate is known.

So, $\ln k$ versus $1/T$, I calculate delta e. Now, if the pore diffusion effects are significant then what is going to happen, see the rate is proportional to root k_n and not k_n its proportional to a into exponential minus delta e by $2RT$. Now, as far as Arrhenius law is concerned, I have this term coming in picture I if I do the same exercise, I am going to get this value delta e by 2, whereas the actual activation energy for the intrinsic reaction delta e right.

Because of this square root the dependency has changed. In fact, dependency is become less sensitive to temperature or other the rate has become less sensitive to temperature the activation energy has come down, simple know what is activation; energy activation energy is something that shows how the reaction is sensitive to temperature. If activation energy is large the reaction is very highly sensitive to temperature. If the activation energy is low a small the reaction is insensitive or very less sensitive to temperature. And

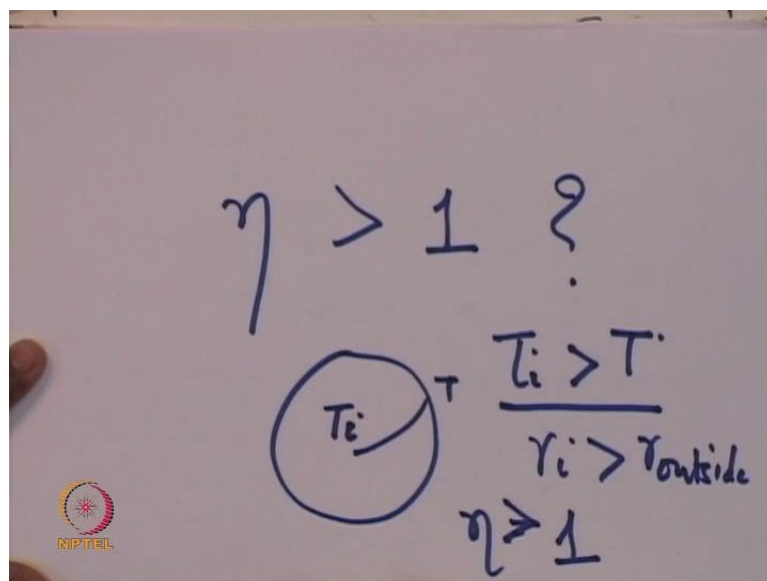
that is what is seen is being observed here, in a presence of pored diffusion effects the sensitivity has gone down.

So, Δe observed is equal to this is observed entire thing, which is equal to Δe actual divided by 2 and I am going to see this, I am going to get a slope equal to Δe by 2 may be noted here, that we are assumed the effective diffusivity to be independent or insensitive to change in temperature. It can change with temperature especially, in the gas phase reactions its bit sensitive to temperature in that case there will be combined effect; that means; the temperature will make influence on not just the intrinsic rate constant, but on the diffusivity as well.

So, this is again 1 more example of falsified kinetics. Falsified kinetics, because of pore diffusion effects. So, kinetics is normally done for intrinsic reaction because all this, but all these effects like pore diffusion later on we going to see external mass transfer. So, they are going to make an impact they are impact and they will change the values of apparent or observed change of value of activation energies or the observed activation energies would be different from the actual activation energy that is what we are seeing.

So, the order and activation energies an like to be different, if are they are going to be different, if pore diffusion effects are there you have to be very careful right falsified kinetics.

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Now can effectiveness factor be greater than 1. Now, from whatever, discussion we had before effectiveness factor has to be less than 1 because the concentration goes down inside the particle diffusion resistance increases. So, the overall rate that we are going to observe is rate calculated at the bulk conditions. So, effectiveness factor which is observed divided by actual rate, actual means the one that is calculated at an external surface.

If that is the ratio then it is less than 1. But, in some cases this effectiveness factor is likely to be greater than 1 and that happens in the case of non isothermal reactions if the heat effects are very large and heat dissipation is not that good. So, I am going to explain it qualitatively just in 2 minutes now and later on will see which the factors which are important are. So, if we have a particle if you have a particle then the concentration reduces as you go inside but see the reaction takes place inside there are thermal effects associated with it.

Heat is evolved, because heat is evolved the temperature inside will go up and if the conductivity of the particle is not enough or not sufficient enough in that case the temperature will not reduce or heat dissociation rate will not be significant. So, the temperature inside a particle T_i and this is t . So, T_i is greater than t is going to be greater than t that is inside a particle the rate is likely to be higher because the rate depends on what the rate depends on concentration and temperature.

So, concentration is going down but the temperature is going up. So, some there is some combination of this concentration and temperature that possible that a rate inside is higher than rate calculated at the external surface. Rate inside is higher than rate outside; that means, effectiveness factor which is ratio of these 2, is slightly greater than 1. And that happens for non isothermal cases if the heat of reaction very large not just that but the heat dissipation also to the outside surface is restricted because thermal conductivity of the particle is not that high.

So, this is the non isothermal case and it is quite likely that you may have effectiveness factor being greater than 1. So, if you do some experiments and get a value of effectiveness factor, observe value effectiveness factor to be higher than 1, do not get perplexed, do not get confused, see were your reactions exothermic or not if the reaction is exothermic; this is quite likely to happen right.

Thank you.

So, we will discuss this further. And solve some examples, if possible.

Thank you.