Chemical Reaction Engineering - II
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Module - 5
Lecture - 21
Internal Effectiveness Factor I

In the last lecture we defined what is an internal effectiveness factor and we started to derive the relationship between the internal effectiveness factor and the thiele modulus. We will continue from there, in this lecture.

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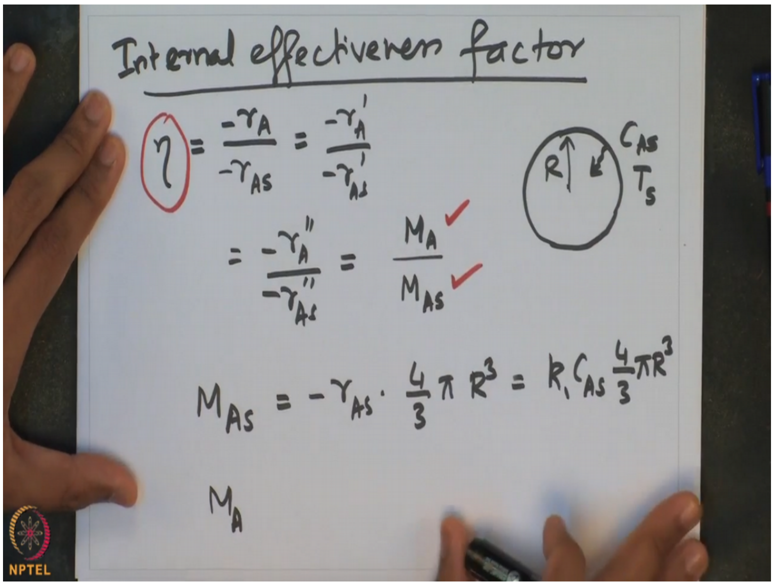

Internal effectiveness factor

$$\eta = \frac{-r_A}{-r_{AS}} = \frac{-r_A'}{-r_{AS}'} = \frac{-r_A''}{-r_{AS}''} = \frac{M_A ✓}{M_{AS} ✓}$$

$$M_{AS} = -r_{AS} \cdot \frac{4}{3}\pi R^3 = k_1 C_{AS} \frac{4}{3}\pi R^3$$

$$M_A$$

So, we concerned a spherical catalyst pellet, where the concentration of the reacting species is C A S at the exterior surface of the catalyst pellet, which is diffusing inside. And there is simultaneous diffusion of the species and the surface reaction which is happening in the catalyst. So, we observed that the, we can define an internal effectiveness factor as a ratio of the rate at which the reaction happens.

The actual reaction rate, divided by the rate at which the reaction happens if the every internal surface is actually at the same concentration as that of the surface. Suppose if the temperature of the surface is T S, then one can say that the r A S, which is the rate at which the reaction happens, if the every location inside the catalyst palette is at the surface concentration and surface temperature.

We also observed that this is = – r A prime by – r A S prime. And that is also = – r A double prime by – r A S double prime; which is basically rate based on the density of the catalyst and this is rate based on the actual surface area which is available for reaction. And that should be = the rate at which the moles of species that is consumed per unit time, divided by the moles of the species that is consumed if the concentration and temperature everywhere inside the reactor is that of the exterior pellet surface conditions.

We also saw in the last class that M A S, which is the rate at which the species reacts if the, if every location on, inside the catalyst is the surface conditions, that is = – r A S into 4 by 3 pi R cube; where R is the radius of the pellet. Now, if it is a first order reaction, then this is essentially = k 1 C A S into 4 by 3 pi R cube. So, if you are able to estimate what is M A, then we are done.

We should be able to find out what is this internal effectiveness factor. If you know, you already know M A S. If we find out what is M A, we should be able to estimate what is the internal effectiveness factor for this particular case.

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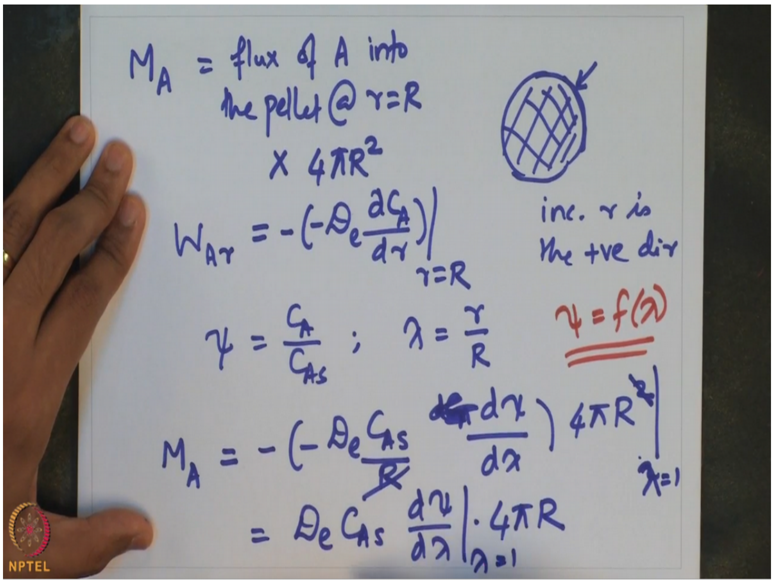

M_A = flux of A into the pellet @ $r=R$ $\times 4\pi R^2$

$W_{Ar} = -\left(-D_e \frac{\partial C_A}{dr}\right)\Big|_{r=R}$

inc. r is the +ve dir

$\psi = \frac{C_A}{C_{AS}}$; $\lambda = \frac{r}{R}$

$\psi = f(\lambda)$

$M_A = -\left(-\frac{D_e C_{AS}}{\cancel{R}} \frac{d\psi}{d\lambda}\right) 4\pi R^{\cancel{2}}\Big|_{\lambda=1}$

$= D_e C_{AS} \frac{d\psi}{d\lambda}\Big|_{\lambda=1} \cdot 4\pi R$

So, let us try to find out what is the actual rate at which the species is actually consumed per unit time when the reaction is actually happening. Now, intuitively, because we assume the steady-state conditions, one can actually think of the total rate at which or the total rate at which the species is consumed because of the reaction. Should essentially be = rate at which the species actually enters into the catalyst pellet at the exterior surface of the pellet.

And clearly, so if I draw a catalyst pellet here. So, whatever is the rate at which reaction is happening inside in this volume, should be = whatever rate at which the species is actually entering from the exterior surface of the catalyst pellet. So, we can take advantage of this aspect and we can attempt to find out what is the actual rate at which the species actually undergoes reaction.

So, let us see how to do that. So, M A is essentially the flux of, let us say species A, into the pellet, @ r = capital R. That multiplied by the exterior surface area which is essentially 4 pi R square. Now, how do we find flux of the species that enters into the pellet at the exterior surface that is r = R. We know the flux equation. We know what is the relationship between the flux and the concentration gradient.

And that is essentially given by W A in the radial direction. Remember that we have assumed that the increasing r is my, is the positive direction. So therefore, the flux at which the species is entering at the exterior surface, is essentially = – D e, effective diffusivity, into d C A by d r, evaluated at r = capital R. Now, we know what is the relationship between concentration and position.

So, suppose if we introduce the dimensionless quantities. Recall that the dimensionless quantity psi is essentially = C A by C A S. And lambda is r divided by capital R. And so, we can introduce the dimensionless quantities here. So therefore, M A is essentially = – of – D e into C A S into d C A, C A S into d psi, divided by d lambda. And that multiplied by 4 pi r square.

So, we can cancel out this. And that should be = D e C A S into d psi by d lambda into 4 pi R. And this evaluated at lambda = 1. This evaluated at lambda = 1. So, we know what is the relationship between psi and lambda. We already know the solution of the equation. So, from that we can actually estimate what is d psi by d lambda. And we can plug in here and find out what is M A. So, psi is essentially given by;

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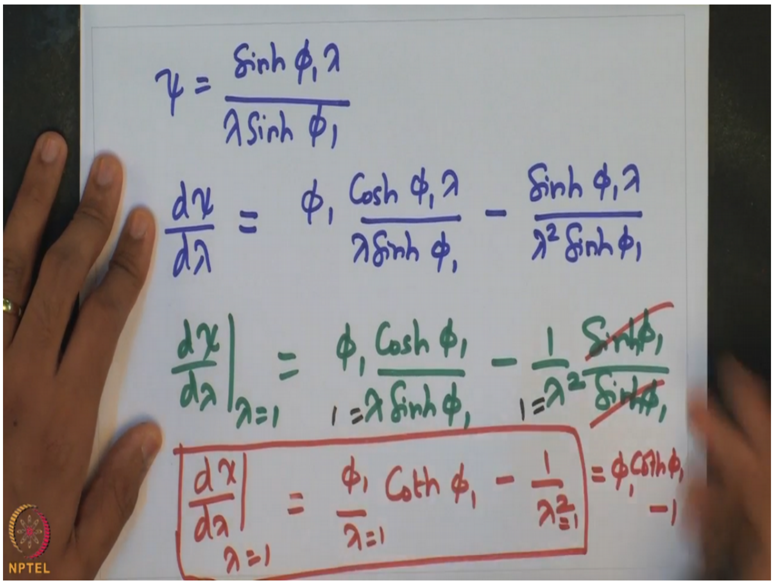

$$\psi = \frac{\sinh \phi_1 \lambda}{\lambda \sinh \phi_1}$$

$$\frac{d\psi}{d\lambda} = \phi_1 \frac{\cosh \phi_1 \lambda}{\lambda \sinh \phi_1} - \frac{\sinh \phi_1 \lambda}{\lambda^2 \sinh \phi_1}$$

$$\left.\frac{d\psi}{d\lambda}\right|_{\lambda=1} = \phi_1 \frac{\cosh \phi_1}{1 = \lambda \sinh \phi_1} - \frac{1}{1 = \lambda^2} \frac{\cancel{\sinh \phi_1}}{\cancel{\sinh \phi_1}}$$

$$\boxed{\left.\frac{d\psi}{d\lambda}\right|_{\lambda=1} = \frac{\phi_1}{\lambda=1} \coth \phi_1 - \frac{1}{\lambda^2 = 1}} = \phi_1 \coth \phi_1 - 1$$

The solution of the equation which we saw in the last class is, sin hyperbolic phi 1 lambda, where phi 1 is the corresponding thiele modulus. Sin hyperbolic phi 1. So, from here we can find out that d psi by d lambda, is essentially = phi 1, cos hyperbolic phi 1 lambda, divided by lambda sin hyperbolic phi 1 – sin hyperbolic phi 1 lambda, divided by lambda square into sin hyperbolic phi 1.

Now, if we evaluate this at lambda is = 1; so, we need to evaluate this expression at lambda is = 1. So therefore, d psi by d lambda at lambda is = 1, is essentially given by phi 1 cos hyperbolic phi 1 divided by lambda sin hyperbolic phi 1 – 1 by lambda square into sin hyperbolic phi 1 divided by sin hyperbolic phi 1. So, these 2 terms essentially will cancel out.

And so, this is = phi 1 by lambda. And cos hyperbolic by sin hyperbolic is nothing but cot hyperbolic phi 1 – 1 by lambda square. So, d psi by d lambda at lambda = 1, is essentially given by this expression here, which is phi 1, thiele modulus corresponding to the first order reaction, divided by lambda, which is basically the dimensionless position, into cot hyperbolic phi 1 – 1 by lambda square.

And we can also substitute lambda. This lambda is essentially = 1. So that is given by phi 1 cot hyperbolic phi 1 – 1. So, recall that, we need to substitute this is = 1 and we have to set lambda square is = 1.

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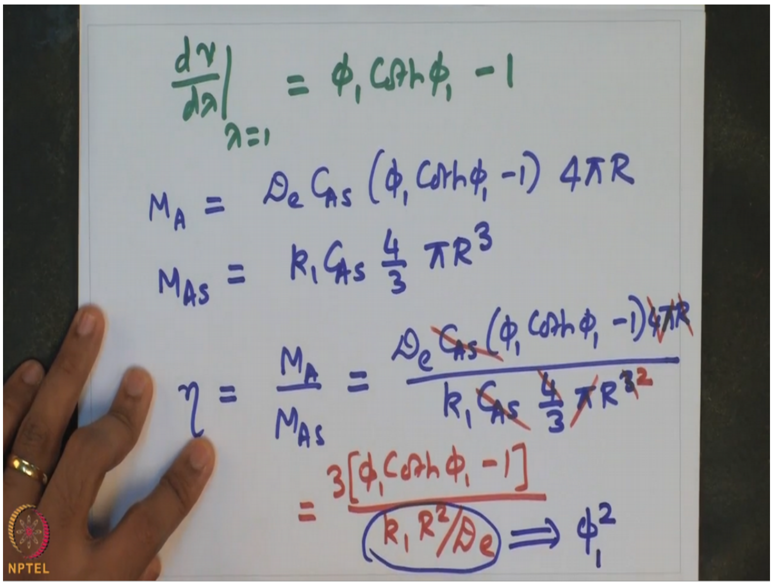

$$\left.\frac{d\psi}{d\lambda}\right|_{\lambda=1} = \phi_1 \coth\phi_1 - 1$$

$$M_A = D_e C_{AS} (\phi_1 \coth\phi_1 - 1)\, 4\pi R$$

$$M_{AS} = k_1 C_{AS} \frac{4}{3} \pi R^3$$

$$\eta = \frac{M_A}{M_{AS}} = \frac{D_e \cancel{C_{AS}} (\phi_1 \coth\phi_1 - 1) \cancel{4\pi} R}{k_1 \cancel{C_{AS}} \frac{\cancel{4}}{3} \cancel{\pi} R^{\cancel{3}2}}$$

$$= \frac{3[\phi_1 \coth\phi_1 - 1]}{\boxed{k_1 R^2/D_e}} \Longrightarrow \phi_1^2$$

So, from here we see that d psi by d lambda at lambda is = 1, is essentially given by phi 1 cot hyperbolic phi 1 – 1. So, this we can substitute in the rate at which the species is consumed. So, that is M A, which is = D e C A S into phi 1 cot hyperbolic phi 1 – 1, into 4 pi R. Now, recall that M A S is essentially = k 1 C A S into 4 by 3 pi R cube. So, thus the internal effectiveness factor eta, is essentially given by M A by M A S.

And that is = D e C A S into phi 1 cot hyperbolic phi 1 – 1 into 4 pi R divided by k 1 C A S into 4 by 3 pi r cube. So, we can cancel out the like terms here; pi goes away. We can cancel out 4. And C A S goes away. And one R we can cancel out. We will get this. So essentially, this is nothing but phi 1 cot hyperbolic phi 1 – 1 divided by k 1 into R square by D e. And that whole multiplied by 3.

What is this term in the denominator? This is nothing but phi square. So, we know that this = phi 1 square, which is for the first order reaction. So, clearly from here we can find out that eta is =;

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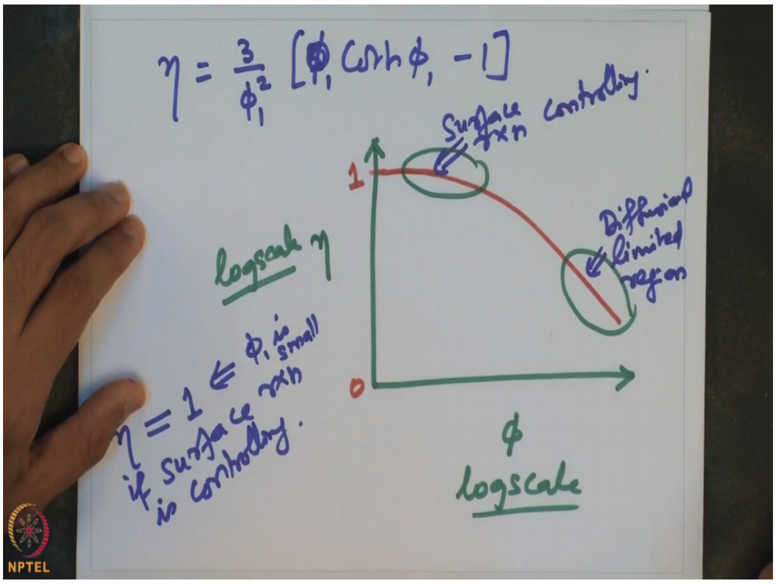

The effectiveness, internal effectiveness factor eta, for first order reaction, for spherical catalyst particle is essentially given by phi 1 cot hyperbolic phi 1 – 1. So, this effectiveness factor relationship with the thiele modulus is actually a very powerful relationship, because this helps in identifying when the reaction is actually surface reaction limited or internal diffusion limited. Suppose we look at, suppose let us say we plot this expression here.

You want to plot this expression, 5 versus eta. Let us say that we are actually plotting it in log scale. Let us say we plot it in log scale. And what is the maximum value of eta as per the definition? So, in the case of spherical catalyst pellet, under isothermal conditions, the maximum rate at which the reaction can happen is actually at the surface condition. If everywhere inside the catalyst pellet it is at the surface conditions.

When there are, when it is a constant density system, where there is no volume changes. So, therefore, eta which is the internal effectiveness factor, essentially it is = 1, if the surface reaction is controlling. If surface reaction is controlling. Now, if surface reaction is controlling, it means that the diffusional limitations are essentially absent. And recall that, if diffusional limitations are absent, then essentially the thiele modulus is actually a very small number.

We observed in the last couple of lectures that when thiele modulus is large, it is essentially the diffusion limitation, diffusional limitations which is controlling the overall reaction rate. And if phi is very small, it is essentially the surface reaction which is actually controlling the overall reaction rate. So, from here, when eta is = 1, essentially it corresponds to the fact that phi 1 is actually small.

So, this corresponds to, when phi 1 is small. So, let us try to plot this eta versus phi. So, eta goes from 0 to 1. Recall, remember that it is log scale. And phi can have any value, starting from very small value to very large 10, 20, 30, whatever number that is. And so, we expect that, close to phi, very small value, the effectiveness factor essentially is, behaves as though it is surface reaction controlling.

So, eta is essentially close to 1, when phi is very small. But then when, as phi increases, the effectiveness factor goes down which means that the diffusion is actually now controlling the overall reaction rate. And the diffusion limitation, so this region is essentially the diffusional limited region. And this region is the surface reaction controlling region or surface reaction controlling region.

Now, so in between these 2 regions, it cannot be said what is actually controlling. It could be both surface reaction controlling or could be the diffusion reaction, diffusion limit. In fact, there will be contributions of both the surface reaction and the diffusional limitation simultaneously, actually controlling the overall rate of the reaction. Now clearly, this picture has a strong implication in terms of the design of the reactor.

So, moment we know what is phi, which is essentially the, essentially given by the properties are intrinsic properties of the reaction and the species that is diffusing. Moment we know that we can actually find out whether the reaction is surface reaction controlling or diffusional limited, diffusional limitations which are actually controlling the overall rate of the reaction.

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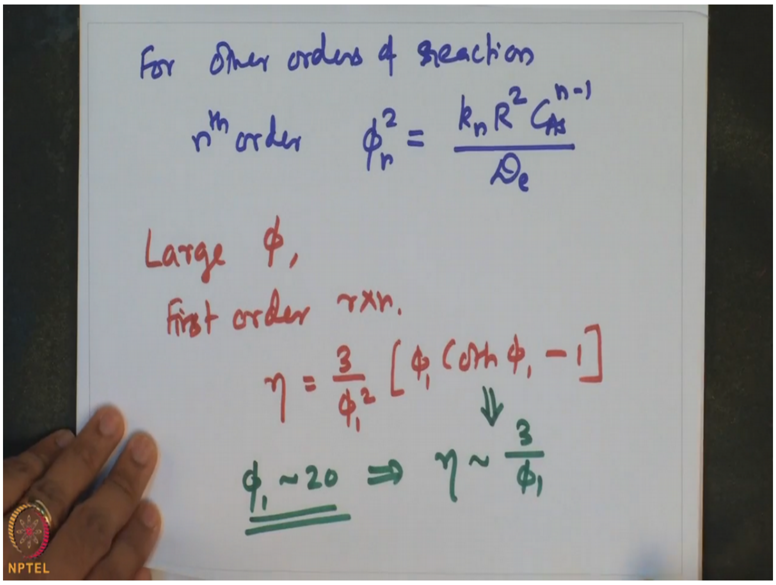

For other orders of reaction

nth order $\phi_n^2 = \frac{k_n R^2 C_{As}^{n-1}}{D_e}$

Large ϕ,

First order rxn.

$$\eta = \frac{3}{\phi_1^2}\left[\phi_1 \coth\phi_1 - 1\right]$$

$$\Downarrow$$

$$\underline{\underline{\phi_1 \sim 20}} \Rightarrow \eta \sim \frac{3}{\phi_1}$$

Now, in principle, the exercise can be done for other orders of the reaction. It can be done even when the reaction is actually second order, third order, or any nth order reaction. So, typically for an nth order reaction, phi n square which is the thiele modulus, square of thiele modulus is given by k n which is the corresponding rate constant, into R square into C A S power n – 1 into the effective diffusivity.

So now, if I try to approximate the values of eta. One can actually approximate the values of eta for large phi, for large phi. Let us say we first considered the case of first order reaction. First order reaction, where eta is essentially given by 3 by phi 1 square into phi 1 cot hyperbolic phi 1 – 1. So, if I now plugin the values of, different values are phi, what we essentially find is that, when the thiele modulus is, let us say approximately 20.

When thiele modulus phi 1 is approximately 20, then the eta essentially scales as 3 divided by phi 1. So, this expression essentially approximates to 3 divided by phi 1. That is the functional form of eta and phi 1 for large values of the thiele modulus. And so, that essentially is what you see in this picture here. For large values of thiele modulus, you will see that it essentially goes as an inverse relationship with the corresponding thiele modulus.

Eta goes as 3 over phi in the diffusion limited regimes. Now one can do this exercise of approximation for an nth order reaction as well. So, let us do that. So, for an nth order reaction;

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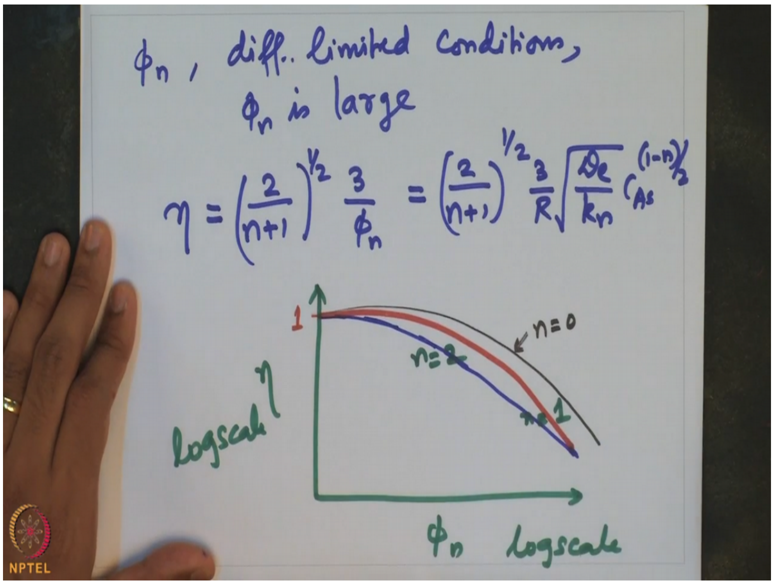

Let us say phi n is the corresponding thiele modulus, for under diffusion limited conditions, that is phi n is large. Then, eta which is the internal effectiveness factor essentially goes as 2 by n + 1, to the power of half, into 3 by phi n, which is essentially = 2 by n + 1, to the power of half into 3 by R, into square root of D e divided by k n, into C A S to the power of 1 – n by 2.

So, for large value of phi, for any nth order reaction, when n is the order of the reaction, eta would essentially still scale as 3 by phi n, except that you now have a premultiplication factor which corresponds to the order of the reaction that you are looking at. So now, one can actually make this plot of eta versus phi. Suppose let us say I plot phi n. And once again I use log scale. So, for a first order reaction, this is the typical curve that you see, for a first order reaction.

So, this is for n = 1. And for a second order reaction, what is seen is that the eta versus phi, still has a similar profile, except that it is actually slightly below the, it is slightly below for the second order case. So, this is for n = 2. And for a 0 order reaction, essentially this is the eta versus phi graph. So, this is for n = 0, which is a 0 order reaction. And this is for n = 1. And this blue line is essentially for n = 2.

So, that is the typical eta versus phi graph for reactions of different order. And this is, and this can be sketched for any order of the reaction using the corresponding expression or relationship between eta and the thiele modulus. So, what is the purpose of finding such an effectiveness factor?

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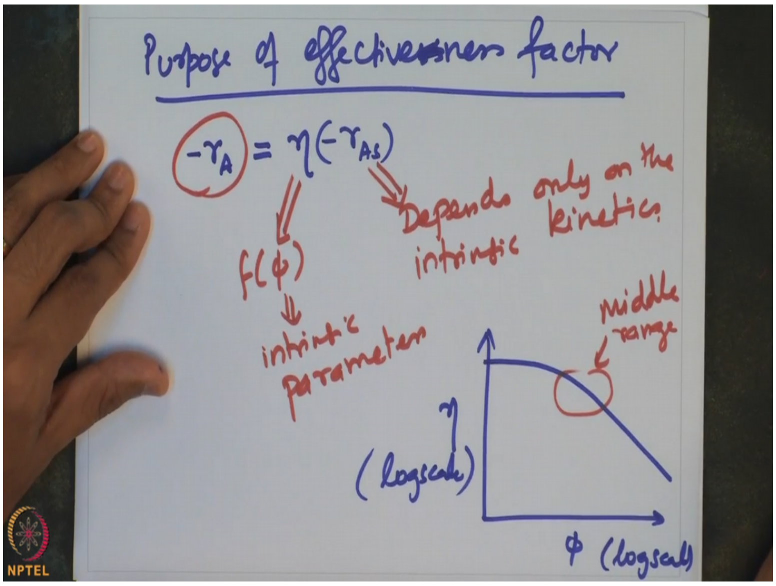

What is the purpose of finding an effectiveness factor? So, if we recall that the definition of effectiveness factor is the actual rate at which all the observed reaction rate to the rate at which the reaction would happen; if every location inside the catalyst has the same condition as that of the surface conditions. So therefore, we can now rewrite the actual reaction rate, as effectiveness factor eta, multiplied by – r A S, which is basically the intrinsic property.

r A S depends on, only on the intrinsic kinetics. So, it is often not possible to measure everything that is happening inside the catalyst. So, if we know eta versus phi and eta, because this can be expressed as a function of the thiele modulus. And thiele modulus is basically a combination of the intrinsic parameters. One can estimate phi using intrinsic parameters. So, for a given system, if we know the intrinsic parameters, we can estimate the theory modulus.

If we know the thiele modulus from the relationship between effectiveness factor and the thiele modulus, we can actually find out what is the effectiveness factor. So, if we know the effectiveness factor, then we can easily predict what is the actual or overall rate at which the reaction is happening, irrespective of what is the regime in which the reaction is actually happening. So, even if it is, even if the reaction is happening; and this is log scale.

So, even if the reaction is happening in the middle range, where we do not know whether it is exactly surface reaction controlling or the diffusion limited conditions. We can still actually find out what is the overall rate at which the reaction is happening, using the relationship from the effectiveness factor; which for most cases for an nth order reaction, can actually be estimated as a function of thiele modulus, which is only a function of the intrinsic parameters.

So therefore, we can actually, simply based on the intrinsic parameters and the intrinsic kinetics, we should be able to predict what is the overall rate at which the reaction might happen for the given conditions at which the reaction is being conducted. And this actually has phenomenal advantage because the rate at which this reaction would happen at surface conditions is controlled by the concentration of the species at the surface.

And we have assumed that the concentration of the species at the surface is = the concentration of the species at bulk, because there are no external mass transport limitations. In that case, if we know the bulk concentration, then we essentially know what is the overall rate at which the reaction is actually happening in the catalyst pellet. And this has strong implications in terms of the design of catalytic reactors.

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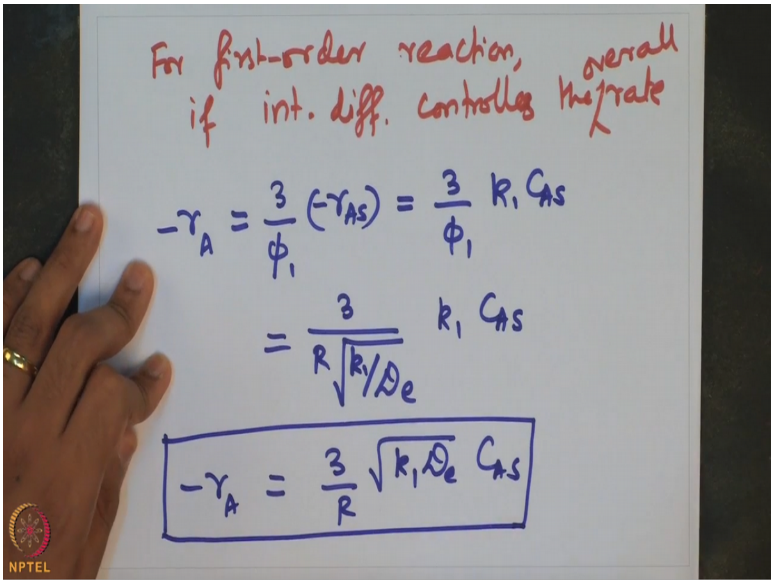

For first-order reaction, if int. diff. controls the overall rate

$$-r_A = \frac{3}{\phi_1}(-r_{AS}) = \frac{3}{\phi_1} k_1 C_{AS}$$

$$= \frac{3}{R\sqrt{k_1/D_e}} k_1 C_{AS}$$

$$\boxed{-r_A = \frac{3}{R}\sqrt{k_1 D_e}\, C_{AS}}$$

So, for a first order reaction case, for the first order reaction case, if internal diffusional limitations exist, controls the rate, controls the overall rate, then we can simply write the overall reaction rate r A, is essentially given by 3 by phi into – r A S. And – r A S is essentially given by 3 by phi 1 into k 1 into C A S where k 1 is the corresponding rate constant. So, from here if we substitute for phi 1, we will see that this is = 3 by R, into square root of k 1 by effective diffusivity, into k 1 into C A S.

And that is = 3 by R into square root of k 1 D e into C A S. So, simply by using the eta versus phi relationship, one can actually find out what is the actual overall rate at which the reaction actually happens. Now, this exercise of finding the relationship between eta versus thiele modulus, can actually be done for different geometries as well. So, we can do the same exercise for a slab geometry. So, what we looked at is basically spherical catalyst.

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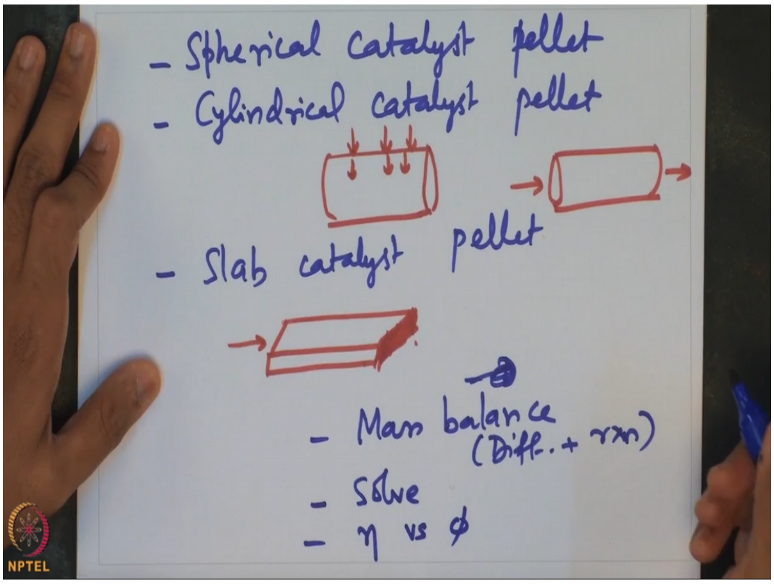

- Spherical catalyst pellet
- Cylindrical catalyst pellet
- Slab catalyst pellet
  - Mass balance (Diff. + rxn)
  - Solve
  - η vs ϕ

What we so far looked at is the, is a spherical catalyst pellet. And recall the example that we saw in one of the lectures where I showed the actual catalyst. The catalyst pellets can be cylindrical in nature; can be cylindrical catalyst pellet. For instance, the cylinder could be at where the species actually is diffusing from the curved surface and radially into the catalyst pellet. And there could be a third case where you have a slab catalyst.

So, we can have a situation where the catalyst is a simple planar geometry. And species actually diffuses in one of the dimensions, let us say. And let us say that we actually, you know seal 1 end of the catalyst. This framework is also applicable when we have a cylindrical catalyst pellet. So, the framework that you developed for slab catalyst where we look at 1 dimensional diffusion and reaction, is applicable for cylindrical catalyst pellet as well, when the fluid species is actually diffusing in the actual direction and the reaction is actually happening anywhere inside the catalyst pellet.

So, if you want to model the slab catalyst, we have to follow the same procedure of writing the diffusion and reaction model. So, the procedure is to write the diffusion, write the mass balance. Basically, one has diffusion + reaction in the mass balance because we assume steady-states. And then we can solve the model. Solve and find out what is the relationship between thiele modulus and phi.

What is the relationship between thiele modulus and the effectiveness factor. And we will see that in the next class. We will see how to find out the relationship between thiele modulus and the effectiveness factor for a slab geometry in the next class. Thank you.