Heterogeneous Catalysis and Catalytic Processes

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Module - 09
Lecture – 28

So, good morning last time I was talking about diffusion through a spherical palette and we have discussed this thing that the flux that is moles of a in or flux into area of cross section Which is 4 phi r square for differential section of the cell and that is 4 phi r s square at evaluated at r s as I said.

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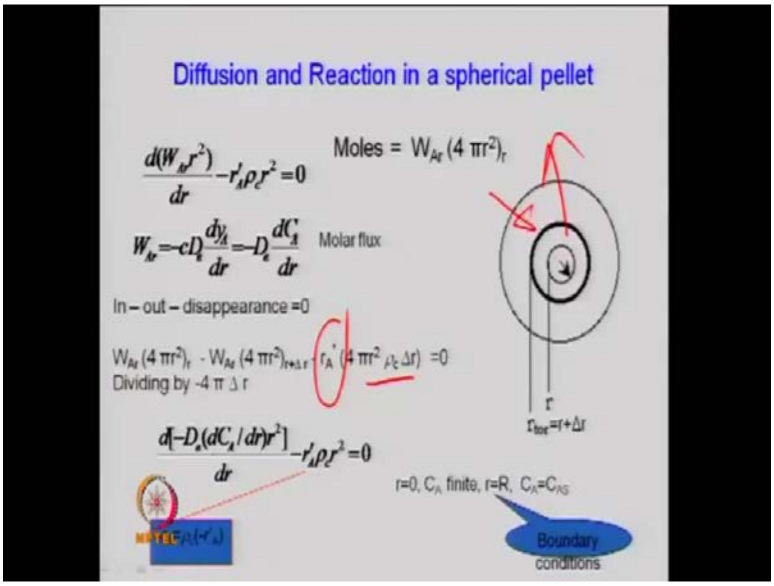

Diffusion and Reaction in a spherical pellet

$$\frac{d(W_{Ar}r^2)}{dr} - r_A'\rho_c r^2 = 0$$

Moles = $W_{Ar}(4\pi r^2)_r$

$$W_{Ar} = -cD_e\frac{dy_A}{dr} = -D_e\frac{dC_A}{dr}$$ Molar flux

In – out – disappearance = 0

$W_{Ar}(4\pi r^2)_r - W_{Ar}(4\pi r^2)_{r+\Delta r} - r_A'(4\pi r^2\rho_c\Delta r) = 0$

Dividing by $-4\pi\Delta r$

$$\frac{d[-D_e(dC_A/dr)r^2]}{dr} - r_A'\rho_c r^2 = 0$$

$r = 0$, C_A finite, $r = R$, $C_A = C_{AS}$

Boundary conditions

We consider inward which is generally the diffusion from outer to inside cell that we are taking the direction outward. So, inward input is at r which is basically 1 can write minus of that flux also. So, W A r into 4 phi r square minus the flux at r plus delta r that is the whole thing evaluated at r plus delta r and minus disappearance because of chemical reaction. So, we have defined here rate of reaction per unit mass of the catalyst. So, multiplied by the mass of the shell. So, 4 phi r square times delta r that is the volume of the shell multiplied by the density of the catalyst pellet.

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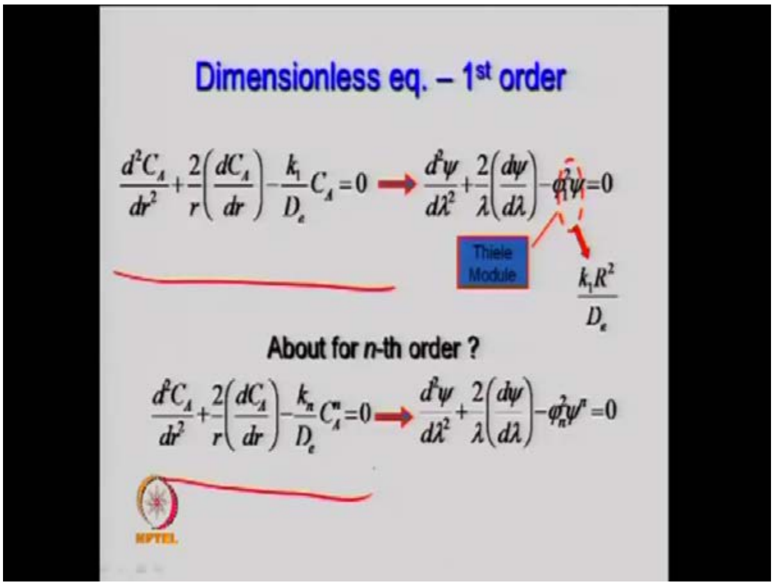

Dimensionless eq. – 1st order

$$\frac{d^2C_A}{dr^2}+\frac{2}{r}\left(\frac{dC_A}{dr}\right)-\frac{k_1}{D_e}C_A=0 \rightarrow \frac{d^2\psi}{d\lambda^2}+\frac{2}{\lambda}\left(\frac{d\psi}{d\lambda}\right)-\phi_1^2\psi=0$$

Thiele Module

$$\frac{k_1R^2}{D_e}$$

About for n-th order ?

$$\frac{d^2C_A}{dr^2}+\frac{2}{r}\left(\frac{dC_A}{dr}\right)-\frac{k_n}{D_e}C_A^n=0 \rightarrow \frac{d^2\psi}{d\lambda^2}+\frac{2}{\lambda}\left(\frac{d\psi}{d\lambda}\right)-\phi_n^2\psi^n=0$$

So, that is the differential equation and if you are simplified where you simply the equation then that come out to be something like what we discussed last time of this form and that have been discussed. So, for any nth order reaction 1 can write minus r a is equal to k C A to the power n and that differential equation is in the form of this k times C A to the power n and we have divided by the diffusion co-efficient. So, finally the differential equation can be written either in this form or for nth order reaction it is in this form. Now, the solution as I discussed can be done numerically using the mathematical tools or analytically just a typical solution we were discussing for analytical.

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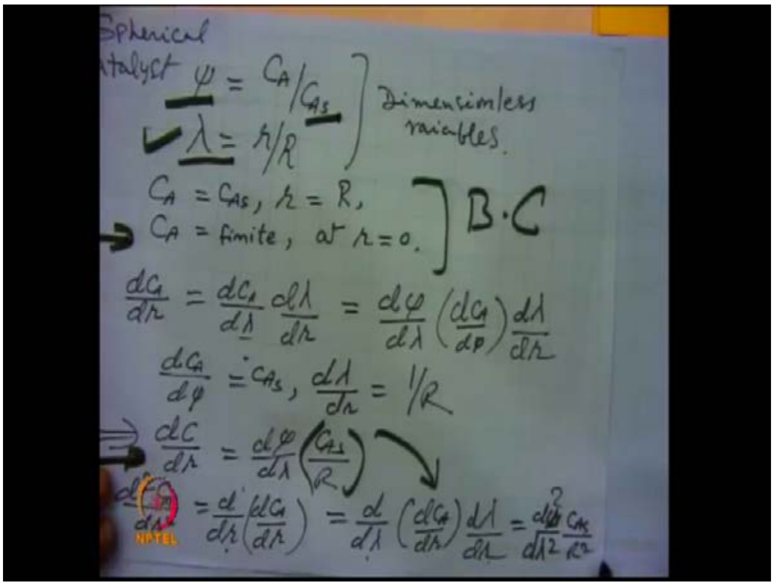

Spherical
talyst

$$\left.\begin{aligned}\psi &= C_A/C_{As}\\ \lambda &= r/R\end{aligned}\right]$$ Dimensionless variables.

$$\left.\begin{aligned}C_A &= C_{As},\ r = R,\\ C_A &= \text{finite},\ \text{at } r = 0.\end{aligned}\right]$$ B·C

$$\frac{dC_A}{dr} = \frac{dC_A}{d\lambda}\frac{d\lambda}{dr} = \frac{d\psi}{d\lambda}\left(\frac{dC_A}{d\psi}\right)\frac{d\lambda}{dr}$$

$$\frac{dC_A}{d\psi} = C_{As},\quad \frac{d\lambda}{dr} = 1/R$$

$$\Rightarrow \frac{dC}{dr} = \frac{d\psi}{d\lambda}\left(\frac{C_{As}}{R}\right)$$

$$\frac{d^2C_A}{dr^2} = \frac{d}{dr}\left(\frac{dC_A}{dr}\right) = \frac{d}{d\lambda}\left(\frac{dC_A}{dr}\right)\frac{d\lambda}{dr} = \frac{d^2\psi}{d\lambda^2}\frac{C_{As}}{R^2}$$

So, we discussed some dimensionless parameters and that was defined like this, what we discussed last time. So, quickly I will go through that that we defined a dimensionless concentration which is defined as psi C A by C A s that is concentration of the reactant species at any point inside the shell and C A s is the concentration at the surface of the catalyst.

So, when you say r is equal to capital R, C A is equal to C A s concentration at the surface of the catalyst. Lambda, a dimensionless radius which was defined the radius at any point divide by the total radius of the palette so that was the lambda. And boundary conditions we defined r is equal to capital R, C A is C A s and r is equal to 0 that is centre of the pellet; c a cannot be infinite. So, the equations say that the C A is infinite it means the constant of the parameter has to be 0. So, C A has to be finite because concentrations decrease from outer to centre of the cell.

So, we just converted this d C A by d r and d 2 c by d r square values in terms of these dimensionless parameters and I discussed that by chain rule. So, d c a by d r is equal to d C A by d lambda into d lambda by d r. So, we defined that here in term of d C A by d lambda because we have already defined here. So, 1 can very easily define C A by d lambda and that is written here in the form of further extension d psi by d lambda because psi is related to concentration times d C A by d psi into d lambda by d r.

So, d lambda by d r can be calculated from here and d C A by d psi can be calculated from here; just by differentiation of this equation. So, we substituted that value and finally, the expression was d C A by d r is equal to d psi by d lambda. Which is now a parameter in the form of dimensionless concentration and the radius dimension and times c s upon r which is the differentiation from here and differentiation from here? Then we evaluated the second derivative d 2 C A by d r square and that is again defined d over d r of d C A by d r that we discussed last time. So, 1 can again write d over d r in the form of d over d lambda into d lambda of d r. So, d C A by d r is calculated here. So, substitute it here in this equation and finally, you have d 2 psi by d lambda square is second derivative of d psi by del lambda d lambda divide times the c s upon r square.

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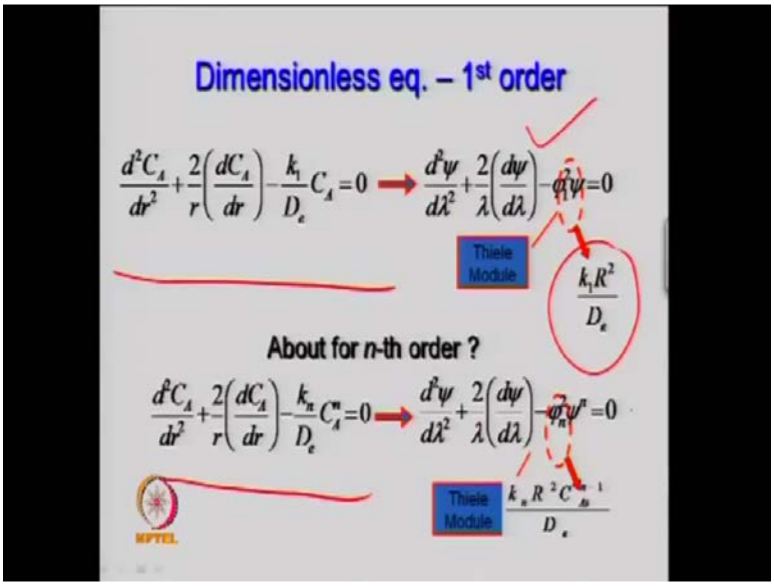

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Thiele Module

$$\frac{k_1R^2}{D_e}$$

About for *n*-th order ?

$$\frac{d^2C_A}{dr^2}+\frac{2}{r}\left(\frac{dC_A}{dr}\right)-\frac{k_n}{D_e}C_A^n=0 \rightarrow \frac{d^2\psi}{d\lambda^2}+\frac{2}{\lambda}\left(\frac{d\psi}{d\lambda}\right)-\phi_n^2\psi^n=0$$

Thiele Module

$$\frac{k_nR^2C_{As}^{n-1}}{D_e}$$

So, that we have seen and discussed last time; so using these dimensionless form we developed the equation in this form which is d 2 psi by d lambda square plus 2 divide by lambda d psi by d lambda minus; we have the term which is k 1 r square divide by D e times psi because we have divided the term all the term here and taken together. So, that became here k 1 R square times D e, which is a kind of parameter and we have defined it as a Thiele Modulus. So, it is the property of the palette and it is a property of the reaction also in fact because order of reaction may affect this value; so that we will discuss in detail later.

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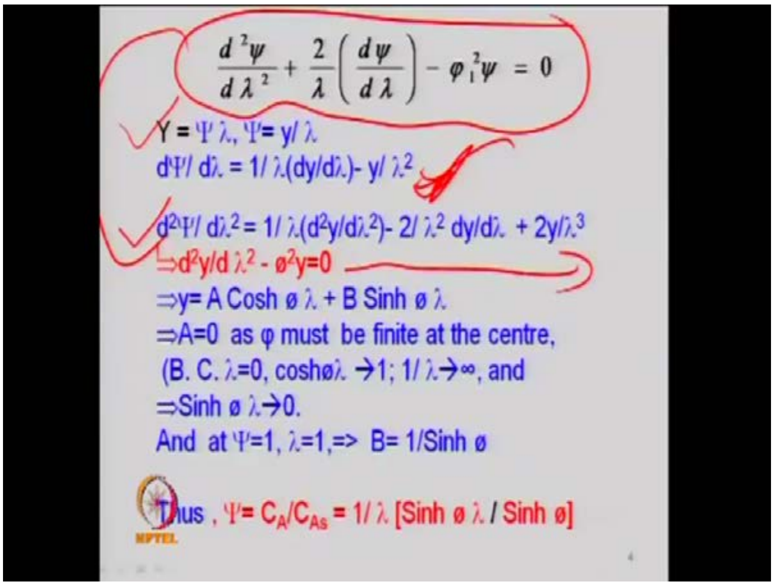

$$\frac{d^2\psi}{d\lambda^2} + \frac{2}{\lambda}\left(\frac{d\psi}{d\lambda}\right) - \varphi_1^2\psi = 0$$

$Y = \Psi\lambda$, $\Psi = y/\lambda$

$d\Psi/d\lambda = 1/\lambda(dy/d\lambda) - y/\lambda^2$

$d^2\Psi/d\lambda^2 = 1/\lambda(d^2y/d\lambda^2) - 2/\lambda^2\, dy/d\lambda + 2y/\lambda^3$

$\Rightarrow d^2y/d\lambda^2 - ø^2y = 0$

$\Rightarrow y = A \operatorname{Cosh} ø\lambda + B \operatorname{Sinh} ø\lambda$

$\Rightarrow A = 0$ as φ must be finite at the centre,

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And at $\Psi = 1$, $\lambda = 1$, $\Rightarrow$ $B = 1/\operatorname{Sinh} ø$

Thus, $\Psi = C_A/C_{As} = 1/\lambda\, [\operatorname{Sinh} ø\lambda / \operatorname{Sinh} ø]$

So, for any nth order reaction also the similar form of the equation can be developed so that is shown here; so in order to solve this differential equation now. So, very quickly I will just go to this that we tried to convert this equation in a simplified form; that is the standard form for analytical solution. But, if 1 can use Bessel functions also for solution analytical solution or 1 can go with the numerical technique as I discussed finite difference methods.

So, we defined a parameter which co-related psi and lambda together; so Y another parameter which is psi into lambda. So, psi can be defined by y by lambda from here. So, 1 can very easily write the value of d 2 psi by d lambda square and d psi by d lambda in the form of y. So, you see here that d psi by d lambda is 1 by lambda times d y by d lambda minus y by lambda square. So, differentiation of this psi is equal to y by lambda where y and lambda both are variable. So, you know the differentiation of this kind first function differentiation of second, minus second function differentiation of the first.

So, 1 by lambda will give you lambda square and minus lambda square and same thing for this it d y. So, first function 1 by lambda differentiation of y so d y by d lambda and minus second function that is your this y and differentiation of the first is 1 by lambda square so that is shown here. Now, do the second differentiation of this, so 1 can very easily find out the value and d 2 psi by d lambda square just again differentiate it again. So, 1 by lambda differentiation of this then d y by d lambda again differentiation of this second function and whatever same thing here for the differentiation of the third function.

So, 1 can very easily do this differentiation. So, just if you substitute the value here in this equation which is now a combination of the 2 terms d 2 psi by d lambda square and d psi by d lambda. So finally, the equation is written in this form which is d 2 y d lambda square minus phi square y is equal to 0 and this equation has very standard format of solution. That is this can be solved just either you write in the form of hyperbolic function which I discussed or in the power of exponential.

So, d 2 y by d lambda square minus phi square y this is a form of differential equation need to be solved for y or psi as a function of y when we write finally, y is equal to psi into lambda. So, you can get the expression in the form of psi and lambda, so this equation simply. What we discussed for pore? So, again I will just discuss to recall that how did we observed that in the pore of a catalyst that the same equation we derived last time for a pore also.

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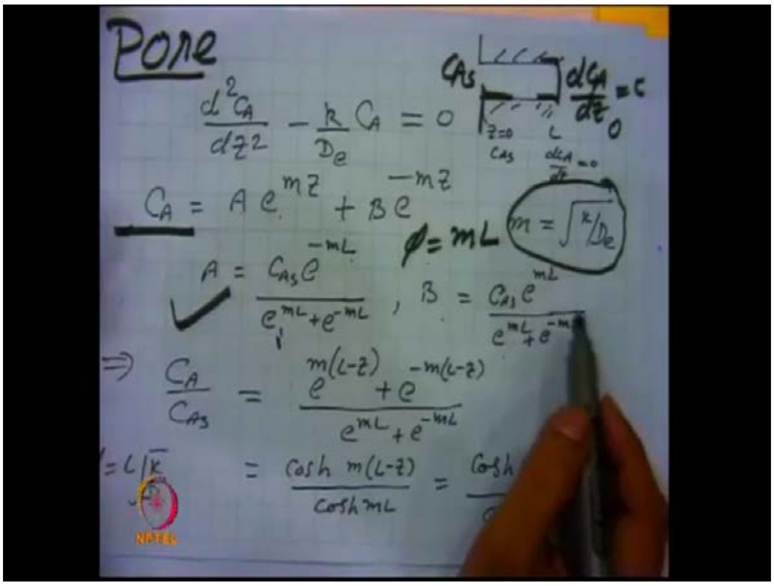

Pore

$$\frac{d^2C_A}{dz^2} - \frac{k}{D_e}C_A = 0$$

$$C_A = Ae^{mz} + Be^{-mz}$$

$$\phi = mL \qquad m = \sqrt{k/D_e}$$

$$A = \frac{C_{As}e^{-mL}}{e^{mL}+e^{-mL}}, \quad B = \frac{C_{As}e^{mL}}{e^{mL}+e^{-m}}$$

$$\Rightarrow \frac{C_A}{C_{As}} = \frac{e^{m(L-z)}+e^{-m(L-z)}}{e^{mL}+e^{-mL}}$$

$$= \frac{\cosh m(L-z)}{\cosh mL} = \frac{\cosh}{}$$

That is that time d 2 C A by d z square minus k by d times C A similar equation here. And the solution of this kind of equation can be written in this form also or in hyperbolic function form. So, from this C A is equal to which I shown in the other form a times e to the power m into z where m is square root of k by d this term and l times square root of k by d is the Thiele modulus again for the pore.

So, this is for a pore but, we have d1 a cylindrical pore model and diffusion in that pore. So, the equation is similar; so C A is equal to a times e to the power m into z plus b times e to the power minus m into z and L can write it in the form of phi also because m into L is your phi. So, phi is m into L where L is this length of the pore so you can write here in the form of phi z upon L and here minus phi z divide by L and the solution of this equation now. Because, I told you that it is a very standard format either you write in this form or you can write here a cosh hyperbolic phi z by l plus b sine hyperbolic phi z by l which is shown here in this form. Solution, based on boundary condition because z is equal to 0, C A is equal to C A s at the pore mouth.

So, here the concentration is known at z equal to 0. Same thing where we have written that at r is equal to capital R, C A is equal to C A s. So, r is equal to capital R means lambda is equal to 1. So, C A by C A s is 1 there. Which is psi? So, if you solve this based on these 2 boundary conditions; then second is your z is equal to l second boundary condition z is equal to l nothing can move here the pores are closed pore is closed from this end. So, here d C A by d z is 0, there we said at the centre the C A is finite, 1 can write d C A by d r is 0 also because of symmetry.

So, this equation which is now second boundary condition d C A by d z is 0 at z is equal to l. So, you have 2 equations 2 unknown. So, A is C A s e to the power minus m L divide by e to the power m L plus e to the power minus m L you need to solve these to solve 2 equations. So, 1 is that C A is equal to C A s at z is equal to 0. So, this becomes A plus B this is 1 this is 1.

So, A plus B is equal to C A s and second time when you are writing z is equal to l d C A by d z is equal to 0. So, differentiate this equation for d C A by d z, so that will give you simply A m e to the power m z minus B m e to the power minus m z is equal to 0 put z is equal to l there; so that will become second equation solve these 2 equation. So, if you solve them then A is equal to C A s e to the power minus m L divide by e to the power m L plus e to the power minus m L and b is equal to C A s cosh e to the power m L plus divide by e to the power m L plus e to the power minus m L. If you remember your hyperbolic functions this is nothing but, e to the power m L plus e to the power minus m L divide by 2 is your cosh hyperbolic function.

So, e to the power theta plus e to the power minus theta is your cosh hyperbolic function not 2 here I think so. And same thing sine hyperbolic theta is e to the power theta minus e to the power minus theta. So, 1 is your cosh function and 1 is you are if it is minus sign that is sine function. So, here these are these are cosh hyperbolic function. So, this is what you have seen here in the form of equation? Either you write in this form or you write in the form of exponential both are same thing because the definition of cosh hyperbolic theta or sine hyperbolic theta can be substituted. So, cosh hyperbolic theta is e to the power theta plus e to the power minus theta sine hyperbolic theta is e to the power theta minus e to the power minus sine minus theta.

So, that if you substitute here so this gives you C A by C A s is equal to e to the power m times L minus z, plus e to the power minus m L minus z, so that time now a plus b values have been substituted divide by e to the power m L plus e to the power minus m L. So, this is your I said earlier this is e to the power m L plus e to the power minus m L.

This is your cosh hyperbolic function same thing here this e to the power m into l minus z plus e to the power minus m into l by z is equal to cosh hyperbolic m of this function. So, that has been written in the form of hyperbolic function and m into l I told is phi Thiele Modulus. So, cosh hyperbolic phi l you take out so m into L is phi. So, cosh hyperbolic phi 1 minus z by l divide by cosh hyperbolic phi. So, this is the expression for concentration profile in a pore C A by C A s.

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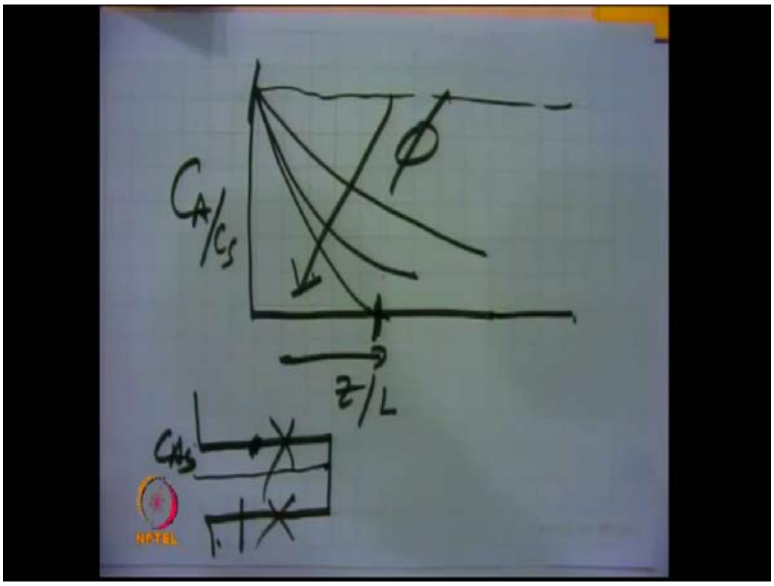

So, if you look at this profile if you look at this profile C A by C As versus if you plot z by L in the pore of that. So, the concentration will drop like this and if your phi is very high it can go like this for increasing value of phi in a pore. So, what does mean high value of phi mean high value of phi mean that means it mean that the reaction is strongly affected by diffusion resistance? So, phi value if high then you can see here the concentration inside the pore drops faster and this simply says that; if you have a pore like this and if diffusion is dominating it may happen if the concentration here is C A s and at this point it becomes 0 at some value of z by L thus concentration is 0 here.

So, it means this action is not being utilized properly there is no reaction because no concentration here. So, it means that is very important when you look at the concentration profile. What you want? You want if the high rate you want then concentration should be uniform everywhere if, the resistance is not dominating then this concentration should be uniform throughout the pore.

So, that is when there is no diffusion resistance phi approaches to 0. So, this is the interpretation of phi value that is diffusion dominating reaction will have high value of phi, which simply says that your concentration gradient inside the pore is very high. So, this is for a cylindrical palette so, same thing is for the spherical cylindrical pore.

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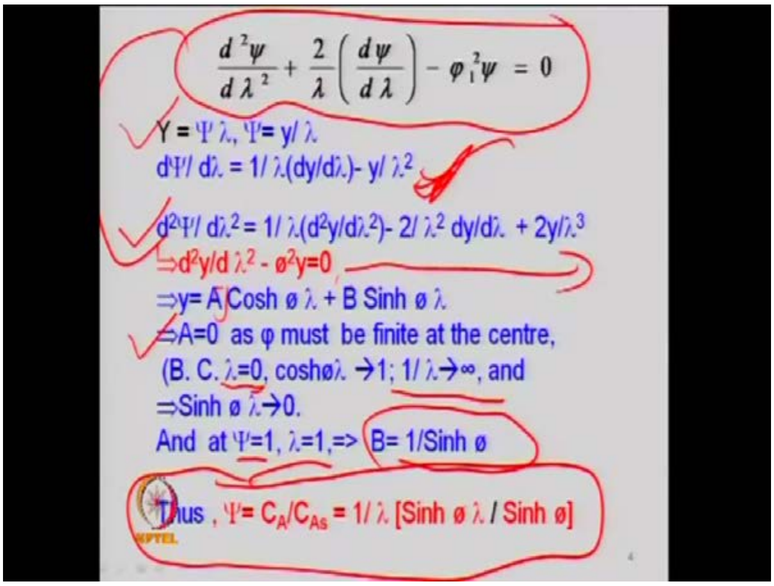

$$\frac{d^2\psi}{d\lambda^2}+\frac{2}{\lambda}\left(\frac{d\psi}{d\lambda}\right)-\varphi_1^2\psi=0$$

$Y = \Psi\lambda$, $\Psi = y/\lambda$

$d\Psi/d\lambda = 1/\lambda(dy/d\lambda) - y/\lambda^2$

$d^2\Psi/d\lambda^2 = 1/\lambda(d^2y/d\lambda^2) - 2/\lambda^2\, dy/d\lambda + 2y/\lambda^3$

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Thus, $\Psi = C_A/C_{As} = 1/\lambda\, [\mathrm{Sinh}\, ø\lambda / \mathrm{Sinh}\, ø]$

Then now it is for spherical palette because same equation you got here solution can be written in the form of either e to the power phi lambda plus e to the power minus phi lambda with these 2 constants or you define it in this form. So, in that case if you're you look at here now boundary conditions have been substituted for finding out the value of a and b that at the centre of the palette that is centre of the palette r is equal to 0 in other way lambda is equal to 0 other terms.

So, your cosh hyperbolic phi lambda will be 1 so lambda is 0 cosh hyperbolic 0 approaches to 1. If, this and sine this 1 by lambda will be approaching to infinite because lambda tends to 0. So, this is very high, so you have 2 terms here in this equation sine hyperbolic phi lambda is 0 so this is 0.

So, here you have 1 by lambda and lambda tends to 0 says that this value is infinite and I told you that at the centre of the palette the concentration has to be finite; low concentration. So, it means this constant has to be 0 this is the first interpretation from the boundary condition. So, this now equation is left only with this term second term because this is 0. Now, same thing for second apply that so, at psi is equal to 1 which is your outer surface of the solid C A is equal to C A s. So, psi is 1 and that time lambda is equal to r by r so r is capital R, so lambda is 1 substitute it here.

Now you have the value of B this is y is equal to psi lambda, so your y is 1 basically here. So, your B will be 1 upon psi sine hyperbolic phi for lambda equal to 1. Substitute these 2 values here in y is equal to psi lambda. So, you have now the expression for concentration profile in the spherical pellet psi which is defined by C A divide by C A s. So, y is psi lambda so that has now been written in the form of psi ca divide by C A s that is the concentration at any point divide by concentration at the surface and that is equal to 1 by lambda in the bracket you will have sine hyperbolic phi lambda divide by sine hyperbolic phi. So, this is the expression for spherical palette concentration profile and you have already seen this expression based on cosh hyperbolic phi 1 minus z by L divide by cosh hyperbolic form so that is in cosh hyperbolic function.

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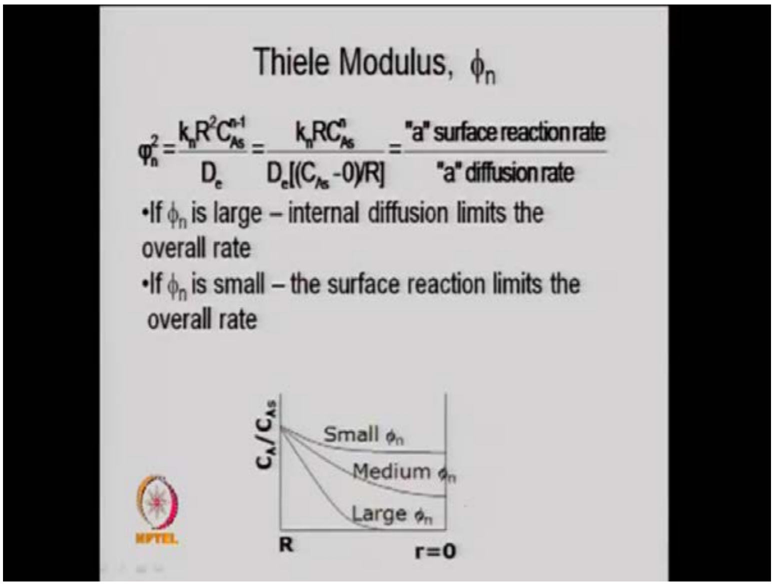

Thiele Modulus, ϕ_n

$$\varphi_n^2 = \frac{k_n R^2 C_{As}^{n-1}}{D_e} = \frac{k_n R C_{As}^n}{D_e[(C_{As}-0)/R]} = \frac{\text{"a" surface reaction rate}}{\text{"a" diffusion rate}}$$

•If ϕ_n is large – internal diffusion limits the overall rate

•If ϕ_n is small – the surface reaction limits the overall rate

So, this is the concentration profile in a palette spherical palette. So, the significance of Thiele modulus which I have already talked. But, if you look at in detail the Thiele Modulus term for any nth order reaction. I defined it for a first order reaction in a pore. So, phi is L under root of k by d this is for first order in a catalyst pore. Now, just try to understand these terms if you look at if I write it in the form of phi square which will be L square times K divide by D. Now, if I try to write it in the form of because, K is the rate constant first order rate constant here and based on volumetric unit. So, if you just look at if I multiply here with phi r square times the L; that is now the volume of the pore.

If I divide it by the same phi r square L there is no change. So, this is now this K and if I just again multiply, just for further understanding C A concentration and here also I just multiply by concentration. Basically, a surface concentration which will be a something constant here. Now, try to interpret the terms. So what you have left? So, L I can remove from here and I can take it in this.

So, 1 l goes like this phi r square, phi r square can be cancelled. So, basically what is this term? This is your rate kinetic rate which is K times C A and I multiply the terms which is phi r square L to total rate, phi r square into L is the volume of the pore and k into C A is C A s is the concentration at the surface. So, that is basically representing the rate of reaction kinetic term a kinetic rate. In the denominator d e D C A by that is D e C A over L if I write it D times C A s minus 0 divide by l and multiplied by phi r square which is here. So, that is flux this is the flux; D C A by d z what you wrote earlier d e D C A by d z. So, this is basically diffusion flux and multiplied by this phi r square that is total moles which have been transported because of diffusion.

So, this is the kinetic rate numerator and denominator is a diffusion rate. So, what is your Thiele Modulus square phi square? If you say for any first order reaction or any general reaction. Now, it is kinetic rate divide by diffusion rate. So, the definition of Thiele Modulus square; that is phi square is defined as the ratio of kinetic rate divide by diffusion rate. In other words I can say it because 1 upon diffusion rate is nothing but, diffusion resistance. So, diffusion resistances divide by kinetic resistance 1 upon k which is indicating the kinetic resistance. So, basically or if you look at the definition of Thiele Modulus it gives you the idea about which term is dominating during reaction whether kinetics is dominating or diffusion is dominating in a reaction.

Same thing this is for 1 more of a catalyst and same definition is extended for any nth order reaction because for first order reaction you observed it K C to the power 0. If you do it the same expression it for the second order reaction; then you will have here C. if third order it becomes 2. So, in general this rate term phi square basically phi square that is k n r square times C A s to the power n minus 1 that is the general expression now for any nth order reaction. What is written here? Divide by D e diffusion co-efficient.

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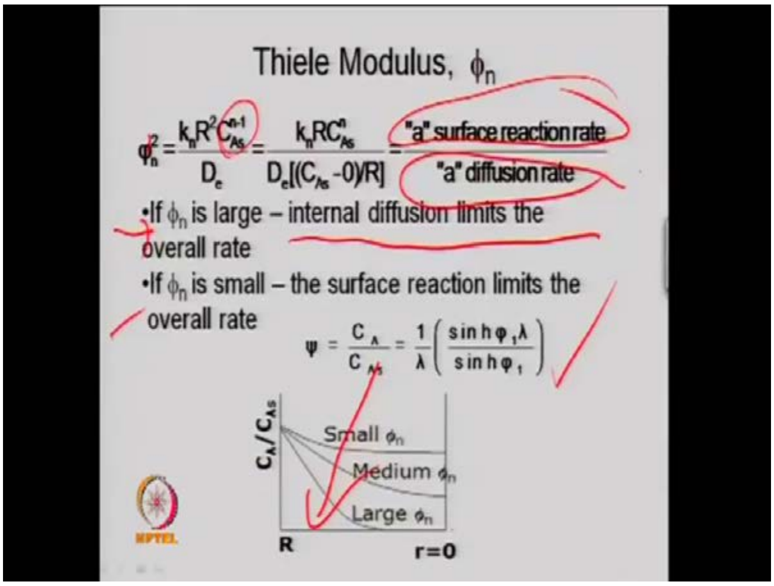

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- If ϕ_n is large – internal diffusion limits the overall rate
- If ϕ_n is small – the surface reaction limits the overall rate

$$\psi = \frac{C_A}{C_{As}} = \frac{1}{\lambda}\left(\frac{\sinh \varphi_1 \lambda}{\sinh \varphi_1}\right)$$

So, this has been just shown here just like what we discussed in this case multiplied or you just take 1 r in the denominator. So, k n R C A s to the power n multiplied by the concentration and divide by the concentration. So, D e C A s minus 0 divide by R diffusion flux, multiplied by the area if you write that will be 4 phi r square in this case. And in the numerator also if you define rate based on surface area you will write down the same surface area 4 pi r square for the pellet.

So, again this definition says it is a surface reaction rate divide by a diffusion rate. That is again the similar definition what you have seen and now phi gives you the idea about the concentration profile in a pore. So, if diffusion is dominating that is means: the phi is large diffusion resistance dominating means your diffusion co-efficient is very small compared to the kinetic term.

That is the numerated term if your reaction is governed by diffusion. So, you know the rate is controlled by slowest step of the reaction. So, if this is the case slowest step of the reaction is suppose diffusion its diffusion co-efficient is very low in that case the phi value will be large. So, generally it is said that for pellet spherical pellet, if phi is more than ten or more than 15 or 20 then diffusion is the rate controlling step. so, 1 can check by because it depends on the r capital R radius of the palette.

It also depends on the concentration when the positive order reactions reaction is positive order then concentration is high then the diffusion may be dominating. That is you have to check that and rate constant will be a function of temperature. So, it means at high temperature it may be possible that kinetics is not controlling; so diffusion may be rate controlled. So, these things can be looked into while doing the experiment and 1 can check the effect of each process parameter.

So, for large phi value means internal diffusion limits the overall rate of reaction that is diffusion controlling reaction and if phi is small this means: that the surface reaction or kinetics control the rate of reaction and 1 can see here the concentration profile. If phi is small then the it is uniform concentration throughout the surface of the solid the concentration will be uniform. So, you will have a higher rate there in that case if it is a positive order reaction.

In this case if the medium then this drops like that if phi is very large, you see that this is the centre of the pellet and this is the outer surface so the concentration changes from C s to a final value 0 where the phi is increasing like this. So, very useful information 1 can get by understanding these effects C A by C A s. we have already defined 1 by lambda sine hyperbolic phi lambda divide y sine hyperbolic phi.

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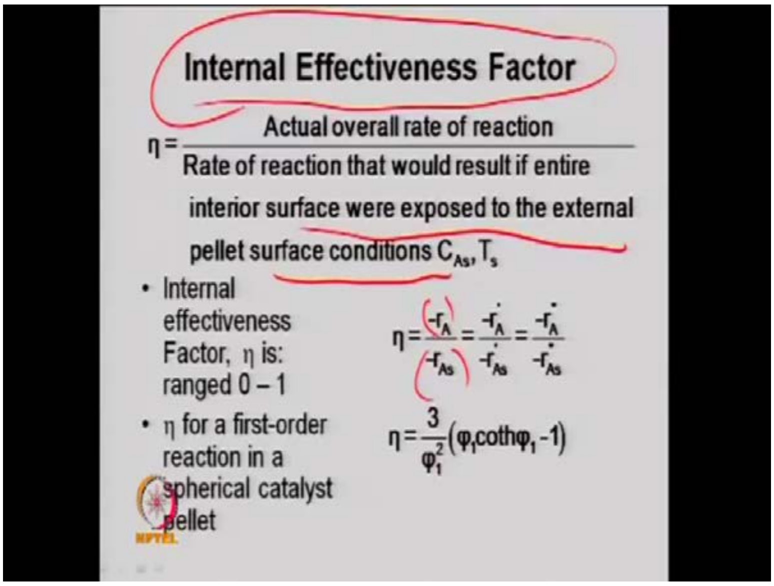

Internal Effectiveness Factor

$$\eta = \frac{\text{Actual overall rate of reaction}}{\text{Rate of reaction that would result if entire interior surface were exposed to the external pellet surface conditions } C_{As}, T_s}$$

- Internal effectiveness Factor, η is: ranged 0 – 1

$$\eta = \frac{-r_A}{-r_{As}} = \frac{-r'_A}{-r'_{As}} = \frac{-r''_A}{-r''_{As}}$$

- η for a first-order reaction in a spherical catalyst pellet

$$\eta = \frac{3}{\varphi_1^2}(\varphi_1 \coth\varphi_1 - 1)$$

Once this I known, so 1 can get the idea how much rate is lowered because of diffusion. That is I said that, when there is a diffusion resistance the rate will lower down how much what contribution is the diffusion resistance. So, 1 can very easily find out that the definition of a term another parameter or parameter of the catalyst. Which is known as Internal Effectiveness Factor? So, here I am saying internal word because it is into the pore of a catalyst or in the solid material diffusion into the pore of a spherical pellet.

So, the definition of effeteness factor it simply says that actual overall rate of reaction divide by the rate of reaction that would result; if entire surface were exposed to the external pellet surface condition. What does it mean? The definition wise it is very clear. Now, here that eta is given minus r A divide by minus r A s. Like this disappearance of which is actually happening and divide by the maximum possible rate of reaction which is measured based on surface concentration or surface conditions. This can be defined based on surface area, based on per volume or mass of the catalyst that has no meaning that is similar. So, if you look at again here for the pore of a catalyst.

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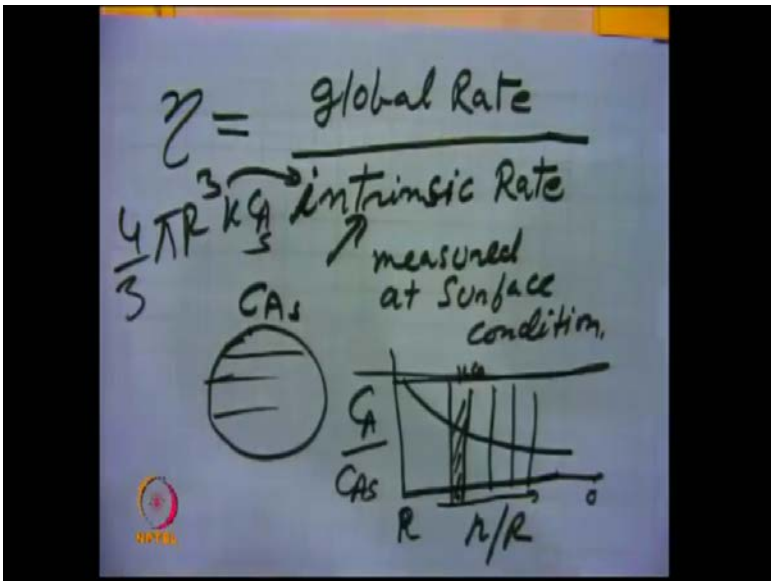

Now, eta is global rate I will say now divide by intrinsic rate intrinsic rate. So, either you say global rate or you say absorbed rate or you say overall rate all terms have same meaning. So, global means absorbed rate what we look actually? When you do the experiment you will get this. This is your absorbed rate; intrinsic rate is basically a maximum rate in 1. I will just little but, change my sentence little later.

But, now I am saying intrinsic is the maximum rate which is measured at the surface condition. So, this is measured at the surface condition. So, basically for isothermal condition this is maximum. But, when the reaction is non isothermal and exothermic then this may not be the maximum I will discuss that later. But, this is your general definition that it is measured under the surface condition or surface condition which is the maximum 1.

See now look at the picture if you here this picture which is a spherical catalyst and here we have written the concentration C A s. And this concentration profile is changing because we have the concentration profile for C A by C A s. That went down something like this. So, this is your r by R which I have written now from this side. So, at the r is equal to r is equal to capital R here and then this is to the centre so 0.

So, if you need to calculate the rate which concentration you will take. So, it means you have to divide it into differential zones assuming something like that what you integrate. For that differential section calculate the rate and then integrate it for the whole pellet. So, it means something which is to be d1 based on the rate at differential c a value suppose you are writing k c a here and then integrate it.

So, k C A for the differential cell which is you know now that you have already done that expression. So, if it is for whole pellet 4 by 3 phi r cube into k times c s if i is a first order reaction. But, if you write it like this then for a differential shell of that sphere that will become 4 pi r square deltas R. So, basically it this rate which you are calculating for a differential section is simply 4 phi r square delta r or d r into C A. So, what will be total rate integrate this for the whole pellet. So, 0 to r and 4 phi r square delta r times minus r that is for a spherical pellet.

So, that will be your actual rate which you have gotten because you know the concentration drops like this. But, what will be this because you are saying it is the maximum rate maximum rate means it when the concentration. So, in 1 way you are saying there is no gradient of concentration maximum rate will be based on this concentration. When you are assuming because now concentration drops.

But, maximum I say it means the concentration C A s throughout measured based on the surface concentration or in 1 way I am measuring the rate at the outer surface of a catalyst pellet. So, that will be simply your 4 by 3 pi R cube times if I assume it is a first order and k C A s this is your maximum rate; intrinsic which I said. So, global rate divide by intrinsic rate that is your refactness factor and for this you have to integrate this expression which is 4 pi r square delta r.

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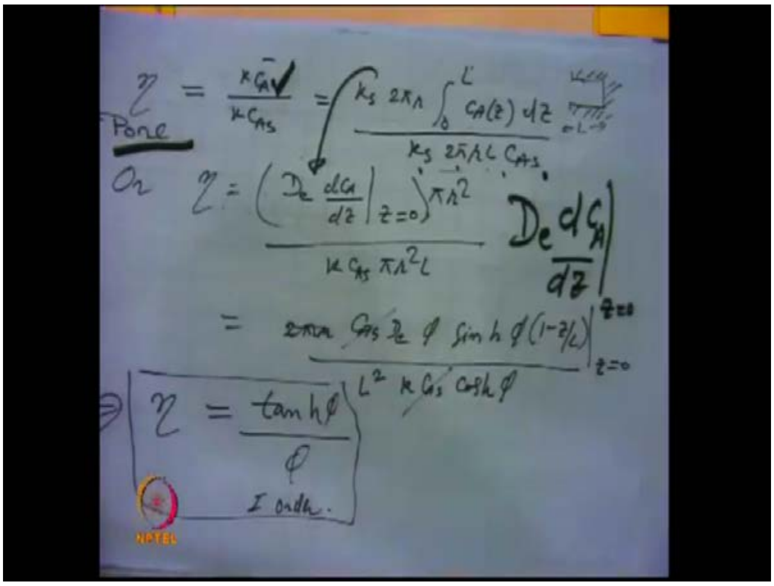

Pore

$$\eta = \frac{k\bar{C}_A}{kC_{AS}} = \frac{k_s\, 2\pi r \int_0^L C_A(z)\,dz}{k_s\, 2\pi r L C_{AS}}$$

Or

$$\eta = \frac{\left(D_e \frac{dC_A}{dz}\Big|_{z=0}\right)\pi r^2}{k C_{AS}\, \pi r^2 L} \qquad D_e \frac{dC_A}{dz}\Big|_{z=0}$$

$$= \frac{2\pi r\, C_{AS} D_e\, \phi \sinh \phi(1 - z/L)\Big|_{z=0}}{L^2\, k C_{AS} \cosh\phi}$$

$$\boxed{\eta = \frac{\tanh\phi}{\phi} \quad \text{I order.}}$$

For doing that just I have shown you for the pore first. Which is again the same thing? For a pore of a catalyst this effeteness factor is again the actual rate divide by the intrinsic rate. So, actual rate which is based on some average concentration C A bar. How will you find that C A bar? By integrating that is overall throughout the surface of a pore because there also concentration changing.

So, here this is you know 2 phi r delta z is the area r is radius of the pore which is constant 0 to L, C A z because concentration is changing with z times delta z which is d z divide by the maximum rate. So, here it is measured based on surface concentration rate is based on surface area otherwise you can write k times phi r square L based on the volume of the pore choice is yours. So, k s time's 2 phi r L times C A s that is the intrinsic rate. So, this is now this is constant either you define based on the volume or you define based on surface area or mass same expression.

So, either you do this integration another option can be because you know at steady state same moles will transport. If you remember if you recall your diffusion equation you have written phi r square d d c a by d z input minus output minus discipline. So, if you say that there is steady state. So, whatever the mole which enters at pore mouth same will go inside and same will react.

So, another thing instead of doing this 1 can do it like this also that is just evaluate d e d c a by d x at z is equal to 0. Which is your pore mouth here? Because whatever the moles which diffuse at this condition the same moles will go inside and they will react; steady state there is no accumulation of mass or reactant species in the pore of a catalyst. so, if I am able to know what is the value of D e d c A by d z this is what written here D e d c a by d z and evaluate that at z is equal to 0. That is you have already the concentration profile C A by C A s, C A by C A s we have already defined like this. So, this is your C A by C A s cosh hyperbolic phi 1 minus z by l divide by cosh hyperbolic phi.

So, differentiate this equation and you will have the concentration in the form of sine hyperbolic phi divide by cosh hyperbolic phi. So, this is what shown here, so evaluate d e d c a by d z at z is equal to 0 multiplied by the flux because this is the flux multiplied by the area of the pore phi r square. So, this is the moles which have been transported into the pore or this will go inside and react. Whatever the concentration profile?

So, either you do from this from here also you get same expression because this is the C A by C A s. So, your C A is simply cosh C A s times cosh hyperbolic phi into1 minus z by L divide by cosh hyperbolic phi. Once again you integrate this it will give you some function of sine hyperbolic and put your limit which are which is from 0 to L. So, again you will get a function of sine hyperbolic phi divide by cosh hyperbolic phi which is tan hyperbolic phi.

So, this is what shown here D e d C A by d z z is equal to 0 evaluated at z equal to 0 times phi r square divide by k times C A s times pi r square. So, here it is based on volume choice is yours as I said so this is pi r square L is your volume of the pore. So, rate constant is based on this k volumetric rate if you define it based on surface area. So, it will become k s C A s times 2 phi r L.

So, I have already told you that k volume is 2 times k s upon r in the last lecture. So, accordingly you can write the expression. So, once you differentiate this d C A by d z because already you have the expression for C A. So, this gives you C A s differentiation of this expression which is here cosh hyperbolic phi L minus z by L. So, this gives you c a s which is already there times D e phi sine hyperbolic1minus z by l differentiation of cosh hyperbolic phi 1 minus z by L will be phi sine hyperbolic1 minus z by L.

So, other terms are already there so that has been substituted in this equation and then you just see here C A s d e phi sine hyperbolic phi 1 minus z by L put z is equal to 0. so, this goal this vanishes out and the other terms which are written I would like to write them in the form of l under root of k by d so phi square is l square k by d.

So, we are just written introduced the term which is already the l is here so we are added and divided multiplied and divided. So, L^2 K C A s divide by De so 1 c a s here also in the you know numerator so cancel.

So, what is this value so this is your phi and this becomes your phi square L L^2 this is k and this D e if you take it is in the denominator now here this is L^2 k by d e this so this is your phi square. So, phi divide by phi square so your affectless factor for a cylindrical palette or for a pore is ten hyperbolic phi divide by phi. So, this is the expression for affectless factor in a pore of a catalyst which is cylindrical pore.

Let us see now, the same expression or similar expression derivation for a spherical palette

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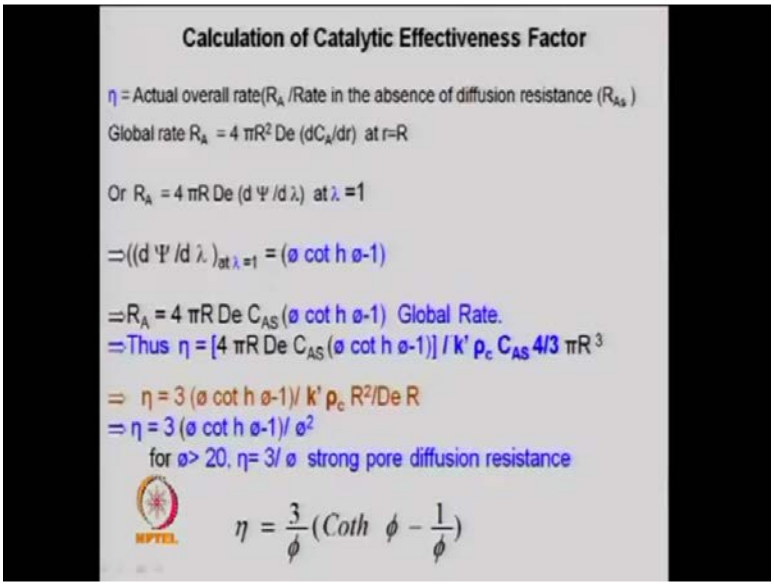

Calculation of Catalytic Effectiveness Factor

η = Actual overall rate(R_A /Rate in the absence of diffusion resistance (R_{As})

Global rate $R_A = 4\pi R^2 De (dC_A/dr)$ at r=R

Or $R_A = 4\pi R De (d\Psi/d\lambda)$ at $\lambda = 1$

$\Rightarrow ((d\Psi/d\lambda)_{at\ \lambda=1} = (ø \cot h\ ø-1)$

$\Rightarrow R_A = 4\pi R De C_{AS} (ø \cot h\ ø-1)$ Global Rate.

$\Rightarrow$ Thus $\eta = [4\pi R De C_{AS} (ø \cot h\ ø-1)] / k' \rho_c C_{AS} 4/3 \pi R^3$

$\Rightarrow \eta = 3 (ø \cot h\ ø-1) / k' \rho_c R^2/De R$

$\Rightarrow \eta = 3 (ø \cot h\ ø-1) / ø^2$

for ø> 20, η= 3/ ø strong pore diffusion resistance

$$\eta = \frac{3}{\phi}(Coth\ \phi - \frac{1}{\phi})$$

So, for a spherical palette also the same approach because the definition is same. So, actual overall rate divide by actual overall rate divide by rate in the absence of diffusion resistance that is global rate, divide by intrinsic rate. So, whatever you know now global rate is defined based on this. Whatever, you understand you know now that global rate is the rate which is measured at the condition which you have actual concentration profile; inside a catalyst palette. So, there is a gradient of concentration because of the diffusion resistance and we need to identify that.

So in that case your global rate R a is defined if you write in terms of flux again choice is yours so the first expression I told you define it integrate the expression. So, global rate because concentration is changing.

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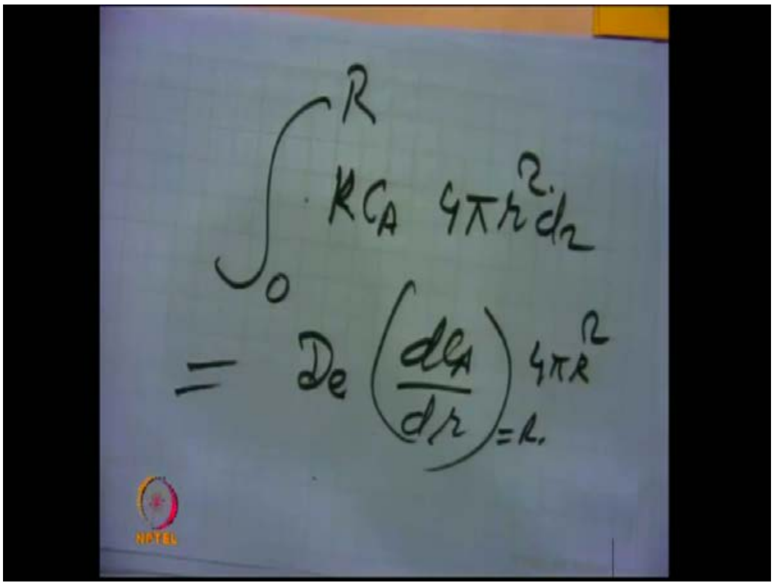

$$\int_0^R k C_A \, 4\pi r^2 dr = D_e \left(\frac{dC_A}{dr}\right)_{r=R} 4\pi R^2$$

So, 0 to r how does it change and you know the rate of reaction, so that will be K times whatever the C A concentration variation rate of reaction; I am defining per unit volume. So, 4 phi r square d r this is the global rate but, I said that whatever moles comes to the surface because of diffusion the same will go inside and react chemically. So, again I can write this global rate by D effective times d C A by d r and evaluate that at r is equal to capital R at the surface of the palette or lambda is equal to 1 and multiply by 4 phi r square.

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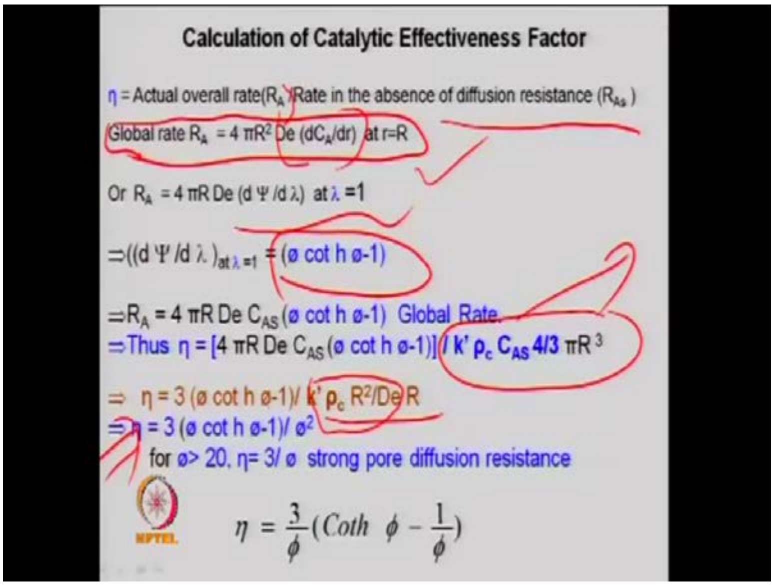

Calculation of Catalytic Effectiveness Factor

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Global rate R_A = 4 πR^2 De (dC_A/dr) at r=R

Or R_A = 4 πR De (d Ψ /d λ) at λ =1

⇒((d Ψ /d λ $)_{\text{at } \lambda = 1}$ = (ø cot h ø-1)

⇒R_A = 4 πR De C_{AS} (ø cot h ø-1) Global Rate.

⇒Thus η = [4 πR De C_{AS} (ø cot h ø-1)]/ k' ρ_c C_{AS} 4/3 πR^3

⇒ η = 3 (ø cot h ø-1)/ k' ρ_c R^2/De R

⇒η = 3 (ø cot h ø-1)/ $ø^2$

for ø> 20, η= 3/ ø strong pore diffusion resistance

$$\eta = \frac{3}{\phi}(Coth \ \phi - \frac{1}{\phi})$$

This is what shown here that 4 phi R square because it is flux times whatever D e d c a by d r and because I told inward r is it is going concentration is decreasing from r capital

R to centre so positive sign can be defined here; so that is what calculated at r is equal to R. So, you know now d C A by d r concentration profile or you can write it in the form of dimensionless parameter because you have already done that. So, d C A by d r can be written in a term of that is what the d psi by d lambda so, that definition if you write.

So, your r gets cancelled, so 4 phi R, D e d psi by d lambda evaluated at lambda is equal to 1. So, now calculate d psi by d lambda from your expression which you have already gotten here in the form of C A by C A s. So, calculate d psi by d lambda or d C A by d r and substitute it so very simple expression. So, differentiation of that equation so d psi by d lambda evaluated at lambda is equal to 1 is simply your phi cot hyperbolic phi minus 1. If you solve and take the limit then this gives you phi cot hyperbolic phi minus 1.

So, your rate is simply R A 4 phi R D e C A s and substitute the value d psi by d lambda so phi cot hyperbolic phi minus 1. So, this is your actual rate global rate so which you can do from here also 1 can check just for your understanding or just as an exercise you do this and get the expression after integration. That is just integrate 0 to r k c a 4 phi r square d r and check.

So, global rate is this intrinsic rate already you know because it is evaluated based on the surface condition. So, either definition whether you define it based on surface area or based on the volume or mass. So, here it is taken in terms of mass so k dash times 4 by 3 pi r cube is the volume of the palette multiplied by density of the catalyst; so this become mass of the palette.

So, basically k dash time’s rho c times this can be written in terms of k v based on volumetric rate constant multiplied by the 4 by 3 phi R cube that you know or that is also equal to 4 phi R square surface area rate constant. So, this is what the intrinsic rate or maximum possible rate for the isothermal case. So, when you take this ratio and simplify again because we want to write this value in terms of phi. So, phi is defined r under root of k by d for order reaction; so just this expression will give you something like k dash rho c times R square divide by D e R. So, this is what we want to write in the form of phi square.

So, this expression is your phi square for the mass rate constant basis. So, k dash times rho c is your k surface oh sorry volumetric rate constant so that can be written. So, if you simplify this so your eta comes out to be 3 upon phi square times phi cot hyperbolic phi minus 1. So, 1 can simplify the expression now for strong diffusion resistance; now you have seen 2 cases for cylindrical palette or pore eta is tan hyperbolic phi tan hyperbolic phi divide by phi.

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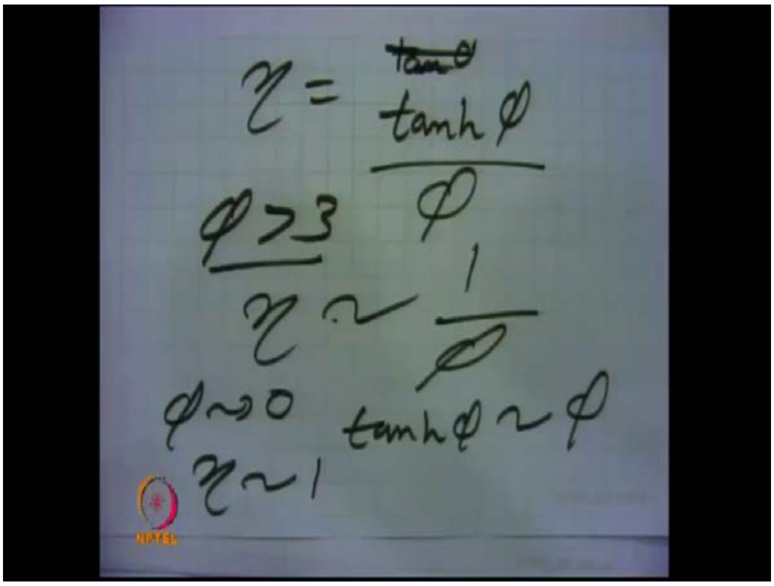

$$\eta = \frac{\overset{\cancel{\tan\phi}}{\tanh\phi}}{\phi}$$

$\underline{\phi > 3}$

$$\eta \sim \frac{1}{\phi}$$

$\phi \to 0$ $\quad \tanh\phi \sim \phi$

$\eta \sim 1$

So, how will you interpret because eta is your effectness factor and eta is something which is in terms of the resistance? which is dominating in the pore of a palette and that can be defined based on eta or phi. If the diffusion is very strong say phi is greater than 3 in this case suppose for most of the cases. So, phi greater than 3 or 5 this tan hyperbolic phi approaches to 1 because you see that value when phi is very large. So, tan hyperbolic phi approaches to 1 just write point9, 9, 9 say like that so eta is just 1 by phi.

So, this shows that strong pore diffusion resistance case this effectness factor is inversely proportional to the value of Thiele modulus. Thiele modulus is simply representing the resistance a kind of diffusion resistance which is dominating in the pore of a catalyst. So, for strong pore resistance this is like defined like this and when phi approaches to 0 no value of phi or less than 3 or phi 1 suppose.

So, then tan hyperbolic phi approximates as phi; if you just calculate from calculator the value of point tan hyperbolic point 9, 9 point 0 3. So, it is similar to the value point 0 3 like that. So, approaches to phi that time what will happen eta approaches to 1. So, and what phi represents phi is representing the kind of diffusion resistance in the pore of a catalyst and we want a kind of this thing because your rate will be high. When there is the minimum gradient of concentration and that can be defined because you know now phi.

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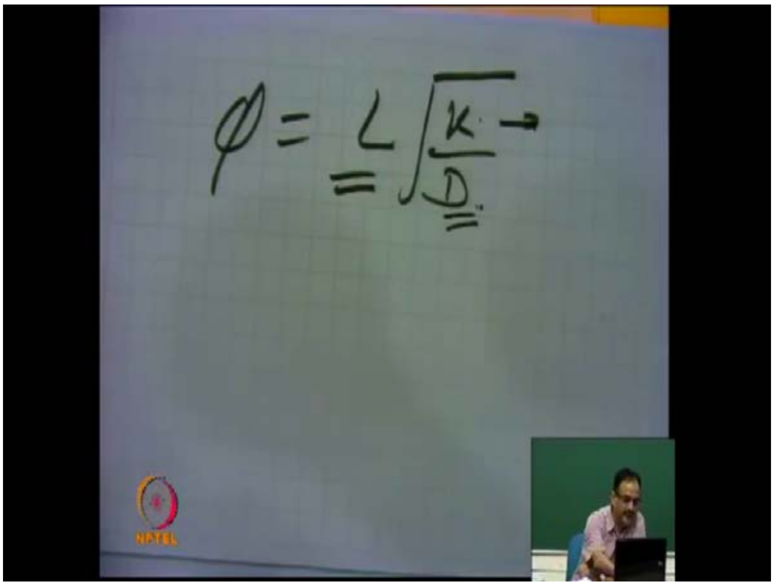

So, phi is something like if I just take this case L under root of K by D first order reaction. So, it means: you make and you have to make you phi small because phi is a term which is representing the contribution of diffusion resistance in a catalyst pore. So, you have to make your phi small in order to get this eta approaching to high value or 1. So, it means: you have to a palette small. So, L is a representation of that characteristic length of the pore. So, basically later on I will talk that L is v p by s x volume of the palette divide by the surface area of the palette. So, your palette should be smaller in size characteristic size of the palette should be small. That is 1 thing; second thing is that k dependency because you need your phi small.

So, when your K is very high that is rate temperature is very high K is a function of temperature. When rate constant is very high then chances are there that diffusion may be dominating; so that is diffusion control. So, temperature should be a control when you look at the kinetic study. So, kinetic control study should be generally done at a lower temperature relative way.

Otherwise, you are the temperature is very high then it may be possible that diffusion may be governing the rate. And diffusion is the design of the palette you have to design the palette accordingly to make the diffusion co-efficient high; wider pore or a defined pore structure. So, this is what the interpretation for Thiele Modulus. So, we have to minimize this diffusion resistance in the pore of a catalyst. So, accordingly design a palette suitably and the same thing has been defined here.

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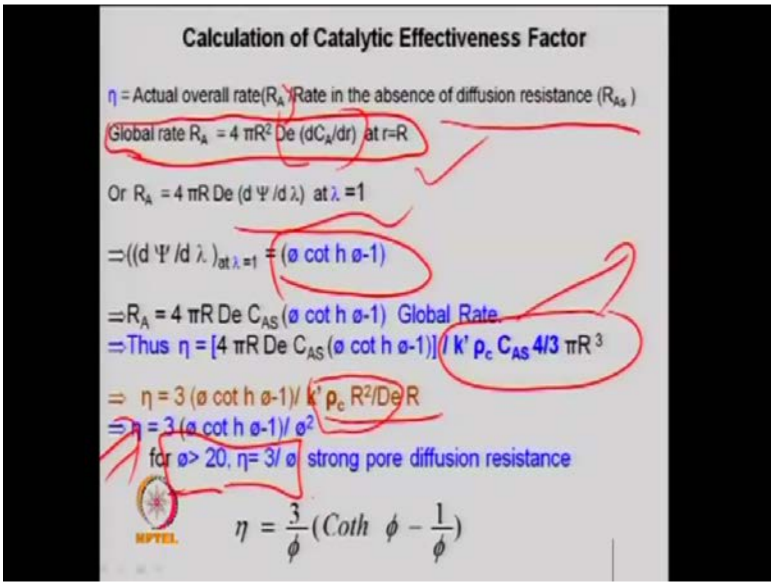

Calculation of Catalytic Effectiveness Factor

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Or $R_A = 4\pi R De (d\Psi/d\lambda)$ at $\lambda = 1$

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$\Rightarrow \eta = 3 (ø \cot h\, ø - 1) / ø^2$

for $ø > 20$, $\eta = 3/ø$ strong pore diffusion resistance

$$\eta = \frac{3}{\phi}(Coth\ \phi - \frac{1}{\phi})$$

When you have a effectness factor phi which is more that is for phi greater than 20 then eta is simply because that time your cot hyperbolic phi this approaches to 1. So, this simply because phi is very large. So, compare to this phi square that is the phi minus 1 which is because cot hyperbolic phi will approaches to 1 for large value of phi. So, then your this phi minus 1 because phi is very large.

So, we just write approximated to phi and so that time your expression that is eta is simply 3 upon phi because this phi and this phi square. So, this gives you just a this value it is just a simple simplified form of expression that for large value of phi then phi cot hyperbolic phi minus 1 that approaches to approximately phi and therefore, the eta is 3 upon 5 strongly that is diffusion controlled resistance and vice versa will be the second case.

That is when the phi s very small then this number can be just written approaches that eta will approach to 1 but, eta cannot be 3. So, basically the phi definition in that case is just R by 3 under root k by d; so that is the different definitions which are available. So, depending upon that value that when the phi value is very low. So, eta approaches to unity rather saying 3. So, this is what the definition of effectness factor what we are written now in either in this form or in this form just 3 upon 5 cot hyperbolic 5 minus 1 upon phi or 3 upon 5 square phi cot hyperbolic phi minus 1.

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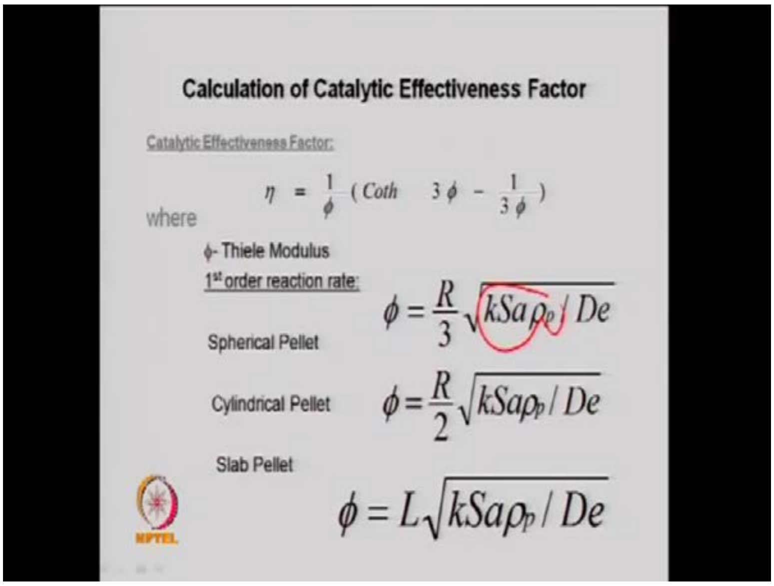

Calculation of Catalytic Effectiveness Factor

Catalytic Effectiveness Factor:

$$\eta = \frac{1}{\phi}\left(Coth \quad 3\phi - \frac{1}{3\phi}\right)$$

where

ϕ- Thiele Modulus

1st order reaction rate:

Spherical Pellet $$\phi = \frac{R}{3}\sqrt{kSa\rho_p / De}$$

Cylindrical Pellet $$\phi = \frac{R}{2}\sqrt{kSa\rho_p / De}$$

Slab Pellet $$\phi = L\sqrt{kSa\rho_p / De}$$

There are some other definitions also available in literature to define phi. So, accordingly your eta definition changes. So, basically here if you see I said phi is equal to R under root k by d where this whole term is your volumetric rate constant k v. when you write it based on surface area it becomes k S times S a times rho p right when you write it in the volume its simply k by D based on volumetric rate constant. S a is your B E T surface area that is what I have discussed. So, this is the B E T surface area meter square per gram, this is gram per centimeter cube. So, this becomes meter square per meter cube, something like that or area divide by the volume, so that is the rate of reaction which is based here on the unit which is.

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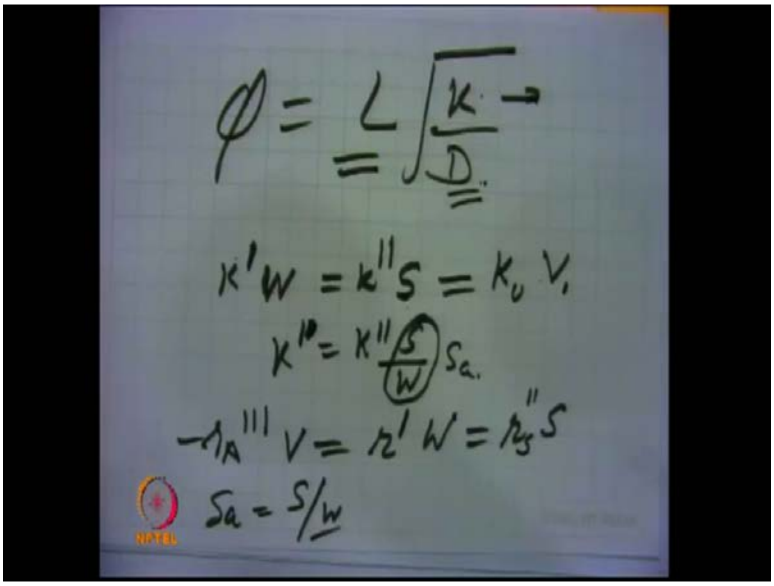

$$\phi = L\sqrt{\frac{k}{D}} \rightarrow$$

$$k' W = k'' S = k_v V,$$

$$k' = k''\left(\frac{S}{W}\right) S_a.$$

$$-r_A''' V = r' W = r_s'' S$$

$$S_a = S/W$$

So, depending upon the type what that I discussed earlier k dash and k double dash that is the this multiplies by the mass of the catalyst will be equal to k double dash time multiplied by the surface area of the catalyst not the B E T total surface area. I am saying and that will be equal to whatever the k volumetric times the volume of the catalyst and now very easily 1 can write if you define. So, generally if I write here S by w so that is your B E T surface area. So, if I write k double dash that is this k or in other words k dash if I write that becomes k double dash times s divide by w; surface area per unit mass of the catalyst when we write it has the unit so that is your S a.

So, k dash is equal to k double dash times this thing. Same thing when you write in this form then this is mass per unit volume of the catalyst, so that is your density of the catalyst. So, 1 can very easily correlate these term or 1 can have a relationship among them because I told you that r a triple dash; which is rate of reaction per unit volume multiplied by the volume of the catalyst is equal to rate of reaction per unit mass of the catalyst multiplied by the mass of the catalyst is equal to rate of reaction per unit surface area of the catalyst or double dash multiplied by the surface area of the catalyst. But, where you report surface area S a that is S by mass of the catalyst you just take care of these units. So, here this is known as V p by s x basically a characteristic length. So, if suppose you have a spherical pellet then the volume of the pellet is 4 by 3 phi r cubes.

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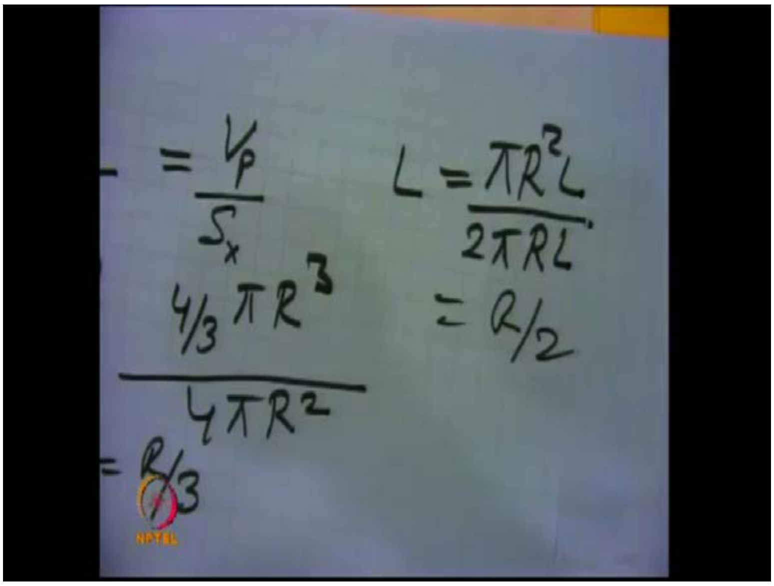

$$= \frac{V_p}{S_x} \qquad L = \frac{\pi R^2 L}{2\pi R L}$$

$$\frac{4/3\,\pi R^3}{4\pi R^2} \qquad = R/2$$

$$= R/3$$

Sometime, this l is known as characteristic length defined by volume of the pellet divide by external surface area of the pellet. So, for spherical palette the first case if you see so 4 by 3 phi R cube this is the volume of the pellet and surface area of the pellet is 4 phi R square. So, this characteristic length comes out to be R by 3. Same thing for cylindrical pellet, this is for Spherical pellet if the cylindrical palette. So, what will be the value? V p phi R square into length volume of the cylinder surface area 2 phi R L. So, this becomes R by 2 sometimes we define this L which is I said in the case of pore it is pore length. But, in rest of the cases it is based on the characteristic length of the palette so that can be defined.

And same thing for a slab or a rectangular geometry that will be depending on the thickness and the whatever the this plane on which through which the diffusion is taking place so area into that depth. So finally, it becomes the thickness of the slab. So, this L is the thickness of that slab through which the diffusion is taking place.

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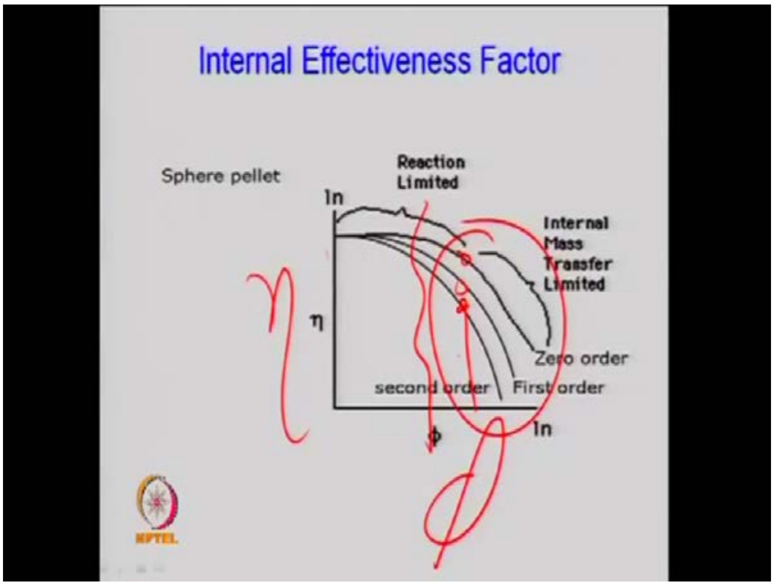

Internal Effectiveness Factor

So, now I have discussed about the effectness factor. So, 1 can see that for a spherical pellet or any pellet in fact the effectness factor eta; which is here as a function of phi that goes like this. So, this value which is at a smaller value of phi that is what I said initial value the eta is nearly 1 approaching to 1 towards 1. So, that indicates that the diffusion is not dominating rather diffusion resistance is not dominating in the rate of reaction so that is for smaller value.

But, when the phi becomes large like that 5, 7, 10, 20 so that time the diffusion is dominating. So, that is known as internal mass transfer control reaction or diffusion control reaction. Also, you if you look at here also you can interpret that when the order of reaction is increasing; the dominancy of diffusion resistance is dominating because it is I told you phi is r under root k c s to the power n minus 1.

So, for first order reaction the concentration is not there but, for other cases the concentration dependency will also be there. So, because the concentration if it is high then you will see some kind of resistance dominant. So, for 0 orders it is on the upper side for if you have same phi value; so can see here this and this. So, effectness factor is higher in the 0 order reaction compared to a second order reaction or first order reaction. So, that is another interpretation that the concentration will also affect the rate for the diffusion governed rates or reactions. So, I stop here and we will continue it next time.