Heterogeneous Catalysis and Catalytic Processes
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Lecture – 27

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Good afternoon. In this lecture I will talk on diffusion through a porous material. And, the last lecture I was just talking about the Bulk diffusion and Knudsen diffusion.

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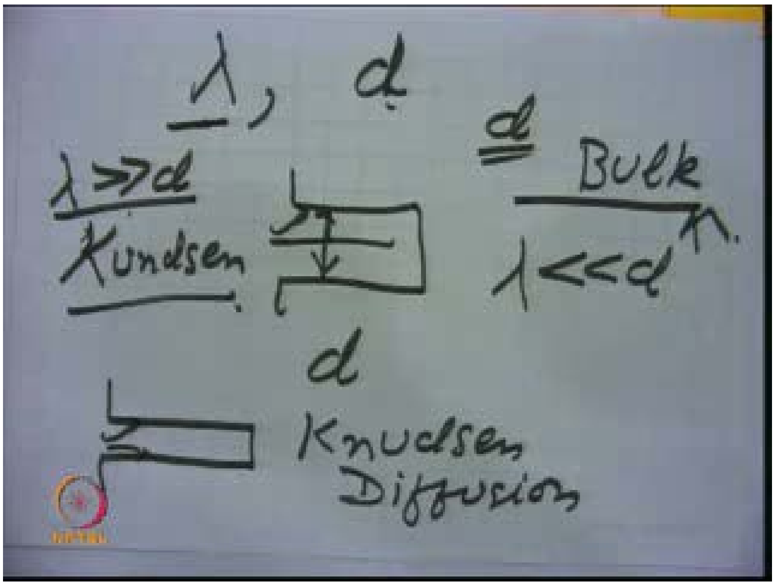

So, 2 types of diffusion that may be dominating in the catalyst pore that is; one is the bulk diffusion which is because of the pore size and the mean free path. So, this is the mean free path which is from the kinetic theory of the gas that is; the distance travelled by a molecule between 2 consecutive collisions. And, pore diameter if I write it size average pore size so, that is; something which we are talking this one the radius or the size of this diameter of the pore.

So, when the molecule diffuses inside or molecule move mass transport through that and they collide among them self, and simultaneously they collide with the pore wall also. So, if this mean free path of the molecule is much greater than the pore diameter so, that will happen when the pores are wider right. The larger pore so, that time the mean free path of the molecule is larger than that is; much higher so what will happen? The molecule will collide among them self right. So, just let me say that in the different way I am just able to change it that, Lambda which is the mean free path of the molecule between 2 consecutive collisions.

And, if this between 2 consecutive collisions if the molecules travel a distance like Lambda, which is less than the pore. So, in one way just basically, the simplicity I would like to say that this if d is pore diameter is wider, larger than the mean free path right then it is Bulk diffusion. So, just to clarify it that when the d mean free path of the molecule right that is, the distance travelled by the molecule is more compared to the pore diameter then the collision between the molecule will be more. In that case so, that time the mean free path is less right.

The distance travelled by the molecule between 2 consecutive collisions is less. So, that time Bulk diffusion is dominating so, it means; when Lambda is less than the pore diameter then the bulk diffusion will take place right. So, that will happen when the pores are wider or in a bigger pore, when the pores are smaller that is; something the second case if the pores are smaller than the mean free path is wider that is; when the molecules are colliding. The distance travelled between 2 consecutive collisions is large compared to the pore diameter.

So, what will happen in a small pore? So, that time the collision with the wall will be more and that is your Knudsen diffusion. So, just to distinguish again what I am saying in small pore you will have the Knudsen diffusion and in larger pore you will have the

Bulk diffusion right. And, that is related to when I say that mean free path so, mean free path is smaller right compared to the pore diameter, which means that is; Lambda is less than the pore diameter so, you will have Bulk diffusion. And, this case is your Knudsen diffusion ok.

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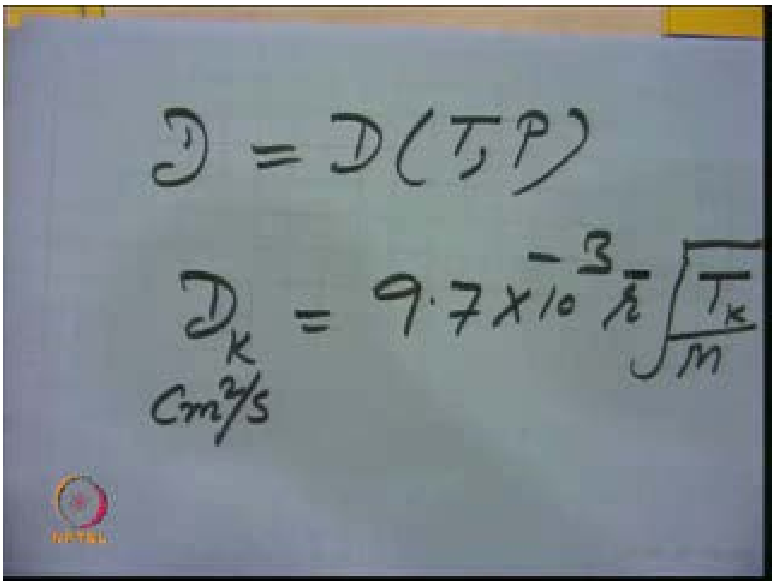

$$\mathcal{D} = \mathcal{D}(T, P)$$

$$\mathcal{D}_K = 9.7 \times 10^{-3}\, \bar{r} \sqrt{\frac{T_K}{M}}$$

cm^2/s

So, these 2 kinds of diffusion are very dominant in the catalyst pore and that will be function of temperature and pressure right. Whereas, Knudsen diffusion is dominating based on as I defined earlier also 9.7 into 10 to the power 3 r bar which is the mean pore radius under root of T divide by M. where T is the Temperature in Kelvin unit which is mentioned here also this one. So, T is temperature in Kelvin M is the molecular weight or average molecular weight of the gas and r bar is the pore radius in centimeter here.

So, D K will be in the unit of centimeter square per second right. So, Knudsen diffusion is dependent on temperature by square root right whereas, this if you look at here; this Bulk diffusion that will be a function of temperature as well as pressure also right. So, temperature if T is to the power 1.75 right, so, there are different correlations for this Bulk diffusion calculation. And, Chapman is for correlation because it depends on the root mean square velocity v r m s as well as, the Lambda mean free path of the gas molecule. So, that is; from your transport phenomena.

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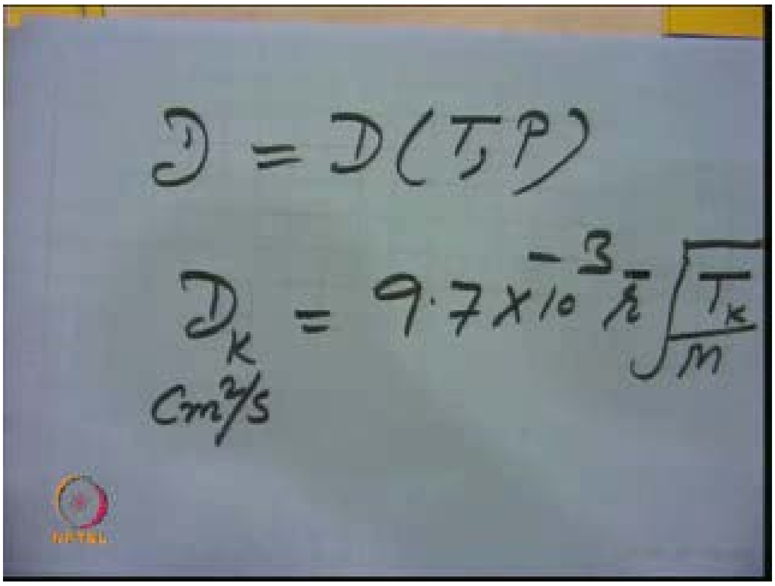

$$\mathcal{D} = \mathcal{D}(T, P)$$

$$\mathcal{D}_K = 9.7 \times 10^{-3}\, \bar{r} \sqrt{\frac{T_K}{M}}$$

cm^2/s

And, when you have these 2 that is; D K and D B by diffusion and, Knudsen diffusion then you can calculate the Combined Diffusivity D C that is known as Combined Diffusivity right. So, Combined Diffusivity is defined based on 1 by D C is equal to 1 by D B plus 1 by D K. So, this is how we define a Combined Diffusivity? Which is a contribution of the Bulk Diffusion Coefficient and the Knudsen Diffusion Coefficient?

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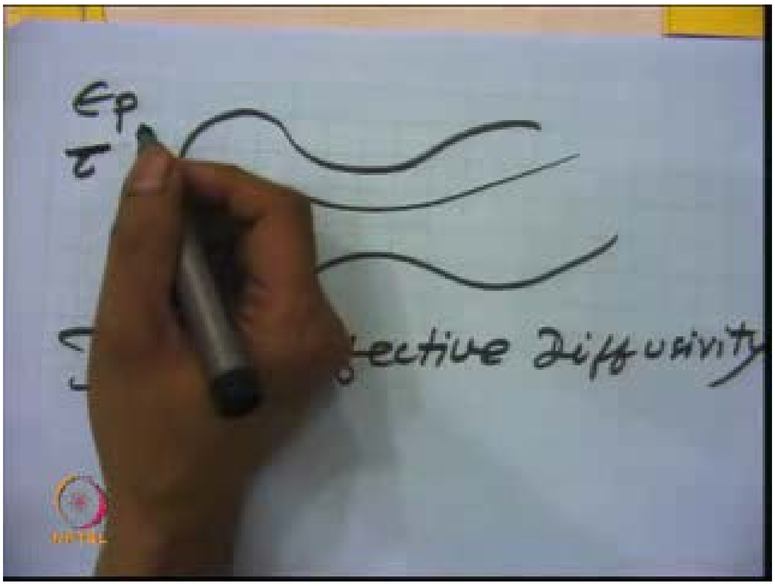

Now, this is just a straight pore when we define a pore which is just single cylindrical right straight cylinder pore. But in general you will see that pores are not straight cylindrical they may be in zig zag path like this; it may be interconnected also right like a Zeolite cage channels they may have channel. So, we need to look at these path that is; the path may be tortuous also it is not in a straight cylindrical you have a defined length right.

So, we define again a term which is known Effective diffusivity. Now, we have Bulk Diffusion Coefficient, Knudsen Diffusion Coefficient and Combined Diffusion Coefficient. And, now, besides that another term which is known as Effective Diffusivity in pore. So, whether you say Effective Diffusion Coefficient or Diffusivity now, this is a contribution of the porosity, because I told porosity may be different epsilon p right. It is depending whether pores are straight cylindrical path which is travelled so, that is; known as Tortuosity right.

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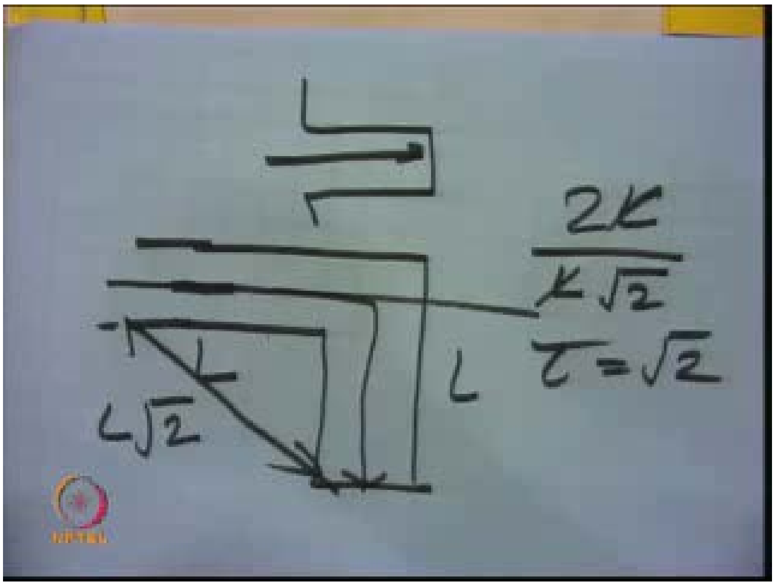

The pores are not straight cylindrical and they may travel a zig zag path right. So, a parameter or a term is required which is known as Tortuosity. And, what is Tortuosity? The definition says actual distance travelled between 2 points divide by the shortest distance between 2 points right. So, actual distance travelled just as an example, a pores are straight and cylindrical like this then the distance travelled actual and straight that is same that is; and shortest is also the same right. But if the pore is suppose just for example, in this shape right then what is the actual distance travelled? Suppose this is both dimensions are in L average dimension this side is L just like right angle here. So, actual distance travelled by a molecule will be this right up to this and suppose like this and shortest distance will be this between 2 points right.

So, shortest distance is L square root of 2. Actual distance is 2 L right. So, 2 L is the actual distance travelled divide by the shortest distance that is L square root of 2. So, in that case the Tortuosity will be just square root of 2 right, just again example but when you see a pore, the pore will be like this so, one has to calculate and these the Tortuosity in a pore can be measured.

It is not difficult to measure, one can measure just by doing the absorption experiments right using Nitrogen gas and pass through that catalyst bed and then one can measure it. So, one can design a set up to look at the Tortuosity of a catalyst. So, once Tortuosity is known porosity is already calculated, porosity definition all of you know pore volume divide by the total volume right. That is; the volume of the pore in a catalyst divide by the volume of the solid material plus volume of the voids right so, this is your porosity.

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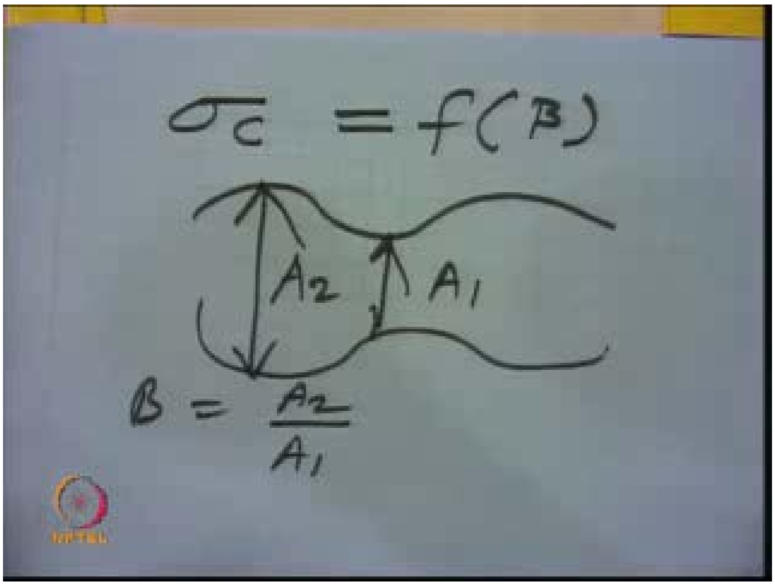

$$\sigma_C = f(\beta)$$

$$\beta = \frac{A_2}{A_1}$$

Another term which is defined is known as Constriction Factor. Constriction Factor that is; related to you what I discussed here sigma C which is a function of Beta. So, sigma C is a kind of Constriction Factor which is defined based on the Beta. What is Beta? Beta is defined whatever I have discussed here, which is given here and defined here also, that is; a function of this area and this area right, that is; the ratio of largest area divide by the smallest area so, that is known as Beta. So, your constriction factor sigma is function of

Beta where this is suppose, you are A 2, this is you are A 1. So, Beta is A 2 upon A 1 right. It is defined here, that Beta suppose; Beta is 1 then sigma is 1 right. This is straight cylindrical pore just like that; the largest area and smallest area both are same right.

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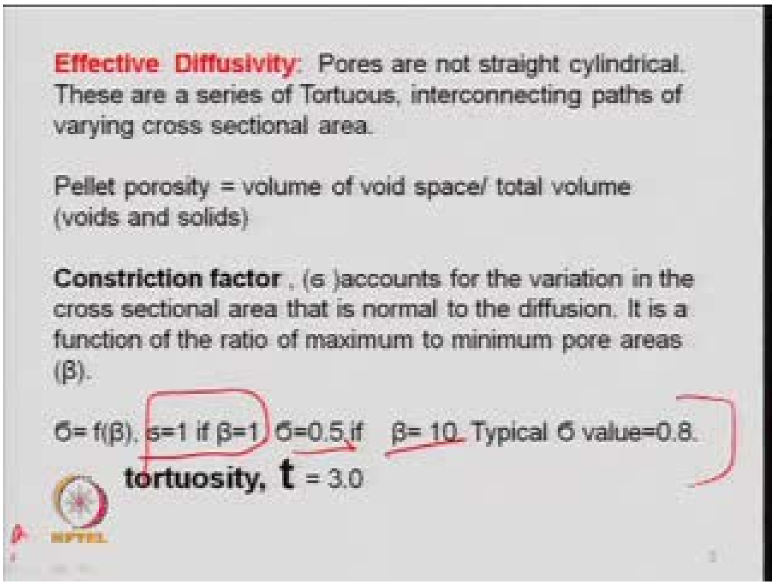

Effective Diffusivity: Pores are not straight cylindrical. These are a series of Tortuous, interconnecting paths of varying cross sectional area.

Pellet porosity = volume of void space/ total volume (voids and solids)

Constriction factor , (σ)accounts for the variation in the cross sectional area that is normal to the diffusion. It is a function of the ratio of maximum to minimum pore areas (β).

$\sigma = f(\beta)$, $\sigma=1$ if $\beta=1$, $\sigma=0.5$ if $\beta= 10$. Typical σ value=0.8.

tortuosity, t = 3.0

And, in rest of the case suppose Beta is 10 then sigma is 0.5. If the typical value which generally, used for the catalyst most of the time we take1 if nothing is defined otherwise sigma is 0.8 Tortuosity is roughly between 3 to 6 right so, these values are generally taken porosity roughly 0.35 or 0.4. So, actual value has to be determined experimentally but if information is not available then the porosity between 0.35 and 0.45 this is; the typical value of a porous material right. And, same thing for the Constriction Factor sigma is generally taken 1. Sigma basically, is nothing but the variation in the cross section area which is normal to the diffusion and is a function of ratio of maximum to minimum pore area.

So, Effective Diffusivity takes care your now, porosity right. So, porosity when I say that is; the pore volume divides by the total volume. Tortuosity which are the pores, which are not straight cylindrical that can be considered by considering this value of Tortuosity and the diameter of the pore may not be uniform throughout. So, you have defined a term which is known as Constriction Factor and then finally, Effective Diffusivity right. So, Effective Diffusivity is defined as now, Combined Diffusivity times, the porosity times, the constriction factor and divides by the Tortuosity right, sometimes most of the time you will see that this sigma C is taken as unity.

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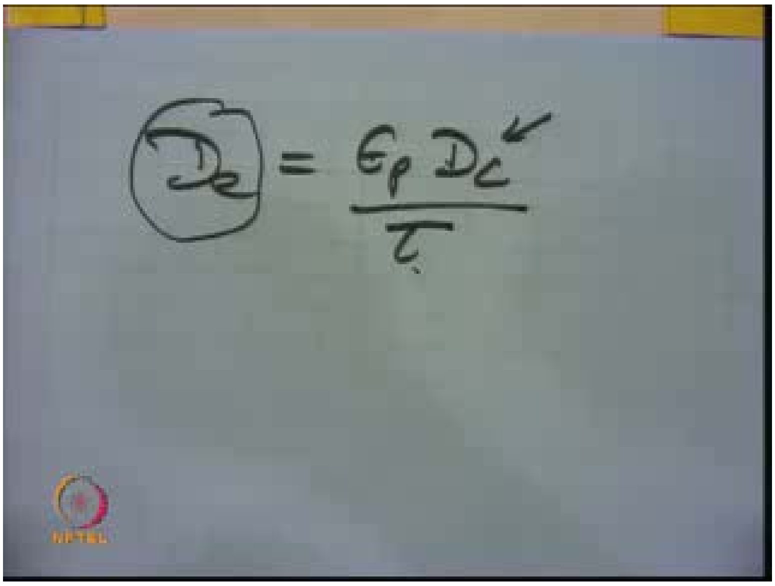

$$\boxed{D_e} = \frac{\epsilon_p D_c}{\tau}$$

So, most of the time we define the Effective Diffusivity D E is equal to epsilon p that is; porosity times whatever, the second term which is your Combined Diffusivity divide by the Tortuosity right so, that is; the definition of Effective Diffusivity. So, whenever we write a Diffusion Equation into a pore of a catalyst this term will be used instead of this right. So, if this is non porous material then you can say that diffusion has no meaning. And, then it can be just you are the Combined Diffusivity, if that contributes in the palette.

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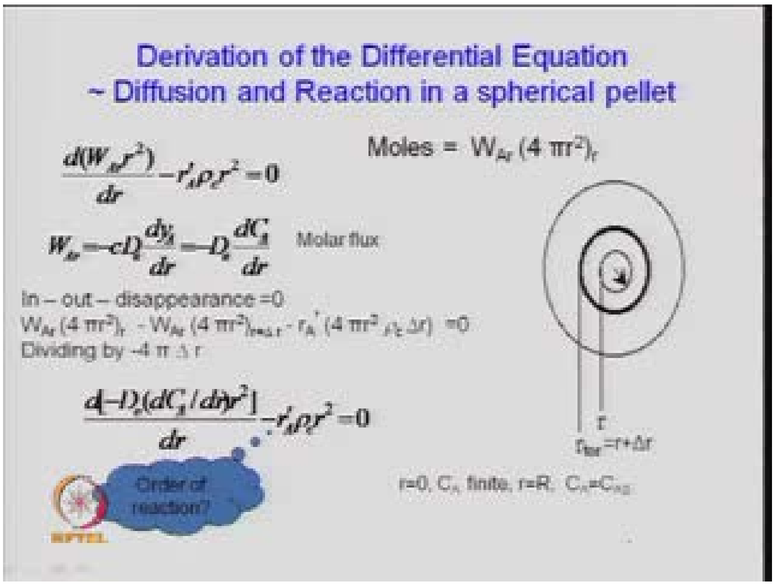

Derivation of the Differential Equation
~ Diffusion and Reaction in a spherical pellet

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

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 $-4\pi\Delta r$

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

Order of reaction?

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

So, once this is known Combined Diffusivity one can write down the Diffusion Equation right. So, this is; the Diffusion or a Formation of a Differential Equation rather than just I will go in the simplified form of the Differential Equation in a spherical geometry. But before going to a spherical palette, catalyst palette one should know what happens in a pore which is straight cylindrical?

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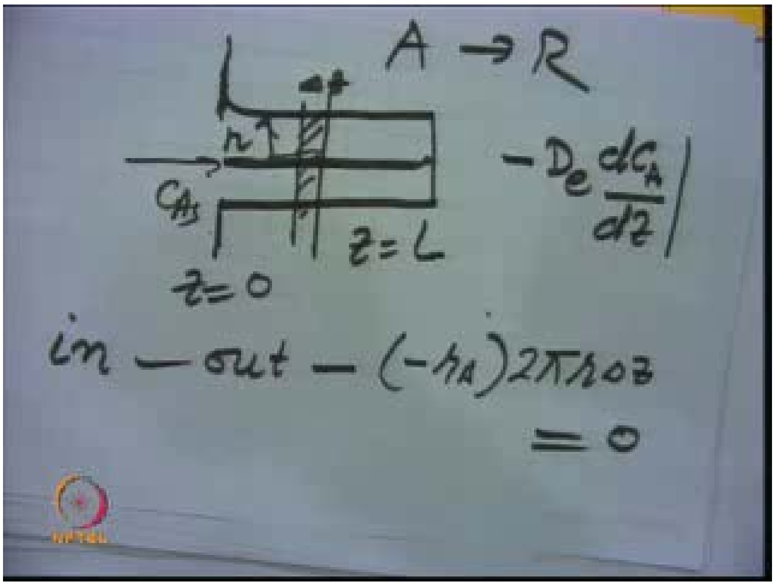

$$in - out - (-r_A)2\pi r\Delta z = 0$$

Diffusion in a straight cylindrical pores right. So, you know that something if I write a radius of the pore r some average radius I am talking a single pore. And, through which the gas species is diffusing right. So, when I say the diffusion it means, you are presuming that the mass transfer contribution which is, from the external surface right or the something which I say that, when it reach to the mouth of the pore, Here; the concentration is known to you. So, this is some kind of boundary condition and this is your z is equal to suppose I say 0, and this is; z is equal to L length of the pore.

So, between these 2 how the points how the concentration change, that will depend on the pore diameter right, small pore or large pore. What I said smaller larger pore so; there will be a kind of concentration profile in the pore right. And, from the understanding or diffusion you know that, diffusion takes place because of the concentration gradient right. So, it means; a concentration profile will be there, and how to find out that concentration profile? In one, because if I am saying that it has reached to the pore mouth and here; the concentration is something like C A S concentration at the Surface of the reactant species.

So, let us consider a single first order reaction. I am just before going for the palette just giving you some idea that, how to write a differential equations in a catalyst pore which is straight and cylindrical. So, single pore right so; what is the equation? You know that now, this is; something given by the fixed law of diffusion because it is governed by the diffusion. So, fixed law of diffusion now will be written D e times d C A concentration of A as a function of Z right.

So, I am assuming that, there is no diffusion in the radial direction everything is diffusing into the axial direction which is your direction z or whatever the convenient dimension one can select. So, this is your flux right multiplied by the area normal to the diffusion. So, pores are this straight cylindrical so, area of this cross section which is pi r square right simple. So, the equation is simply input minus output as disappearance because of chemical reaction. So, minus r A which is based on your choice; so, surface reaction support right.

So, in a differential section of that pore you can write the balance here. One can write the complete pore but since, you are writing that concentration profile so, it is changing because diffusion and chemical reaction. If there is no chemical reaction there, this term will not be here right. So, minus r A suppose if I define it based on per unit surface area choice is yours. Now, if you define it based on per unit surface area and this dimension is say delta Z; so, surface area of this differential section right. This is something like that input here, if you have taken a differential section you cut it and the reaction will take place on the surface of the solid this.

So, that will be r A into 2 pi r delta Z right. Basically, the area of this solid surface section on which the reaction is taking place on the surface right. So, circumference multiplied by the thickness of that so, this is your surface and disappearance what I say and that is 0 because you are writing steady state. So, standard differential equation or mass balance equation remains same that is input minus output minus disappearance because of chemical reaction is equal to 0.

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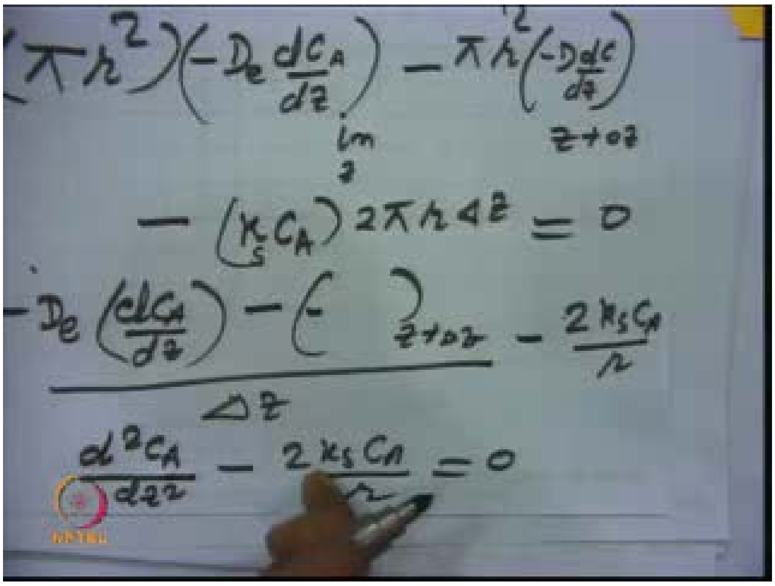

$$(\pi r^2)\left(-D_e\frac{dC_A}{dz}\right)_{in\ z} - \pi r^2\left(-D\frac{dc}{dz}\right)_{z+\Delta z}$$

$$-(k_s C_A)\,2\pi r\Delta z = 0$$

$$\frac{-D_e\left(\frac{dC_A}{dz}\right) - \left(\quad\right)_{z+\Delta z}}{\Delta z} - \frac{2k_sC_A}{r}$$

$$\frac{d^2C_A}{dz^2} - \frac{2k_sC_A}{r} = 0$$

So, if you write it now so, what you will get? Simply pi r square pore radius times minus D e d C by d Z of A in this at Z minus same thing that is; pi r square times minus D d c by d Z, at Z plus delta Z right in minus out, minus disappearance. So, let us assume a first order so; K times C A right concentration which will change down the length of the pore, K times C A so this is; based on surface reaction so, I will write it subscripted as K S, see one can write based on volume. If it is; volume then it will be pi r square delta Z right. Area of cross section into Z and Z .If I write based on surface area so it is; 2 pi r delta Z so, times 2 pi r delta Z is equal to 0 right.

So, everything if you look at this r is the radius of the pore so constant. So, one can very easily divide this equation and, take the limit Z tends to 0 as usual for the formation of the differential equation. So, this equation which is now; you can cancel because this is a constant here, it is not in radial direction. Otherwise, this will not be cancelled but this case it can be cancelled because r is the radius of the pore and there is no flux, no change in that direction.

So, basically what is the equation you have is; if I just cancel it this or divide it by pi r square so, I have minus D e d C A by d Z at Z minus the same thing, at Z plus delta Z minus this will be 2 r K S times this delta Z is equal to 0 right. So, I can divide by delta Z and take the limit that then it will become minus D e d C A by d Z minus this is; at Z the same thing evaluated at Z plus delta Z divide by delta Z right.

And, the second term is your 2 times K S C A divide by r so, what is left here? Z and Z plus delta Z right, so ultimately; the equation has come in the form of simply you check it d 2 C A by d Z square minus 2 K S C A upon r is equal to 0 right. f at x plus delta x minus f at x this is; minus D e d C A by d Z; so, this minus this that is, your d 2 C A by d Z square minus 2 K S upon C A r is equal to 0. This is diffusion equation in a straight cylindrical pore having radius r right. So, now if you want to check the concentration profile in a pore of a catalyst you can very easily solve this equation.

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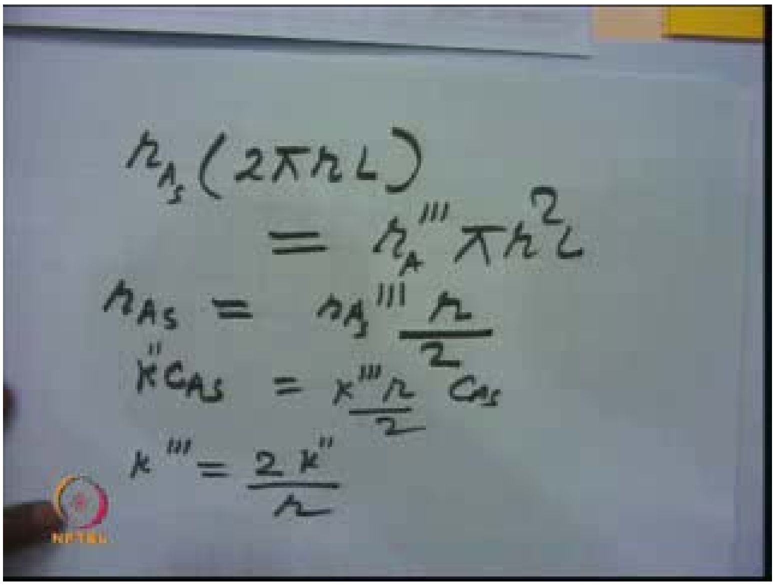

$$r_{A_s}(2\pi r L) = r_A''' \pi r^2 L$$

$$r_{As} = r_{A_s}''' \frac{r}{2}$$

$$k'' C_{As} = k''' \frac{r}{2} C_{As}$$

$$k''' = \frac{2k''}{r}$$

Let me, check the relationship between K S surface reaction rate constant and volumetric. Because you should know that also, say how do you define rate? That is; either based on per unit surface area of the catalyst or per unit volume of the catalyst or per unit mass of a catalyst right. Suppose, if I have written here, in terms of per unit surface area this means, this is the moles reacted per unit that is; moles reacted per unit time, per unit surface area of the catalyst. So, what is the surface area? Here, the catalyst is 2 pi r L right just for one pore I am talking, so this is; basically n times 2 pi r L which is your surface area in one way when you define it per unit mass.

So, this is now total moles which have been reacted that is; moles reacted per unit time, per unit catalyst into the per unit surface area so, multiplied by the surface area so moles reacted. And, if you can correlate it based on r A triple dash which is based on volume right. So, per unit volume of the catalyst so, what will be here; unit pi r square L for 1 pore if I just do.

So, what is the relationship between these 2 is equal; so, r A S is equal to simply if you check here, r A triple dash into r divide by 2 right, the other terms gets cancelled. And, if I say that this is a first order rate; so, this is K times C A S based on surface concentration. And, that is also same thing; so this is K S, basically, I will write it a double prime right.

Because this mass zip this is; rate constant based on surface area and this side it is based on K triple dash into r divide by 2 times C A S. So, what is the relationship between rates constant based on surface area and volume? I can write that K triple dash is equal to 2 times K which is based on surface area as I would write K double dash or you write K subscripted at S divide by r right.

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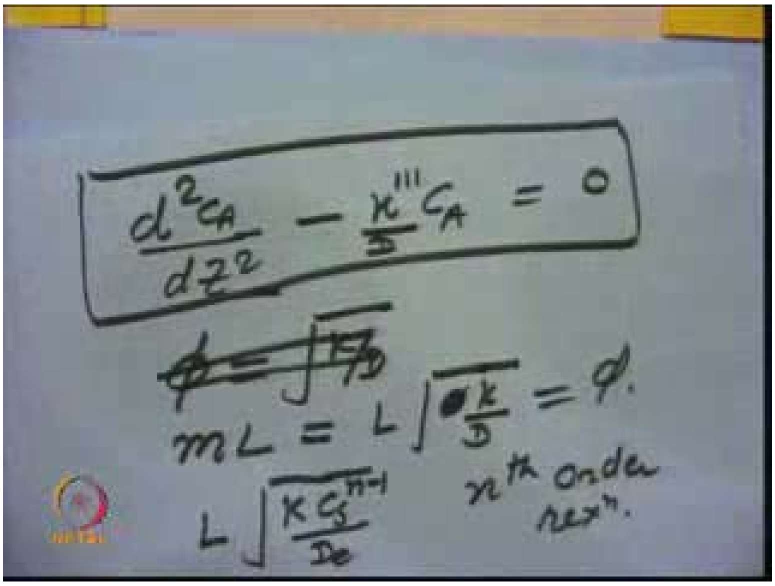

$$\boxed{\frac{d^2 C_A}{dz^2} - \frac{k'''}{D} C_A = 0}$$

$$\cancel{\phi = \sqrt{k/D}}$$

$$mL = L\sqrt{\frac{k}{D}} = \phi.$$

$$L\sqrt{\frac{K C_s^{n-1}}{D_e}}$$

So, in that case what is your equation now which is earlier this one so, I can write this in this form also d 2 C A by d Z square 2 K S upon r can be written based on K triple dash or v rate constant based on volume unit now, times C A is equal to 0. So, this is a kind of differential equation which you must have read many times right and, solution of this equation, differential equation is known. Either you write in the form of hyperbolic function right A1cos hyperbolic say m z. If I just say define some phi sometimes what we do, I missed 1 term here which is D e so that, D e is always here right so, this becomes here so d will if you add d so that is; d times this so, I will write it k by D right. So, diffusion coefficient is always there throughout. So, now this kind of equation can be solved and, this if you remember or if you just see phi is defined Thiele modulus which is your K by D for this case right. And, L is again here so, L under root K by D I will write here, so that is; again 1 term here, length of the pore which is missed here.

So, that is; 2 pi r L so, delta Z which is written here. So, that is fine right so 2 pi r L which comes here, so here it is this L will be 2 pi r L into pi r square L so, that is fine right. So, that is what phi is defined basically, we need a term here, which is just I will write not phi. But phi into L I will define basically, just over the conclusion, m into L a term which is defined by L under root of K by D here. And, this I am talking as phi Thiele modulus right. So, the meaning of this that what if I write the equation in terms of phi I can very easily this term which is defined L under root K by D is a kind of dimensionless number right.

And, this talk for any n through order if I write L under root of K C S to the power n minus 1 divide by D e this is for any n order reaction. I just come back to this point again but just to give you the idea here. So, this equation which we have defined based on this K S surface order rate constant 2 K S upon r that has been substituted and finally, you have the rate which is defined in this case here. which is defined in your original equation somewhere here that is; what we were defining K S into C A into 2 pi r Z and finally, you have the definition of phi we find like this right.

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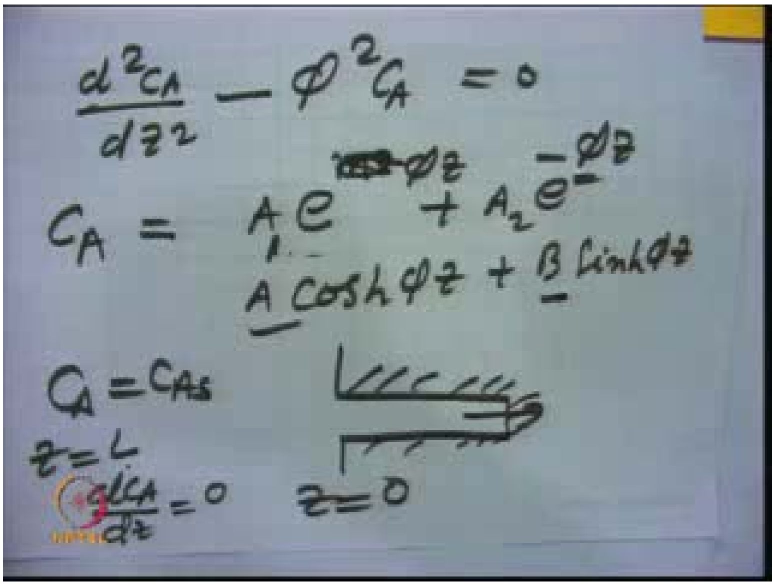

$$\frac{d^2C_A}{dz^2} - \phi^2 C_A = 0$$

$$C_A = A_1 e^{\phi z} + A_2 e^{-\phi z}$$

$$\underline{A}\cosh\phi z + \underline{B}\sinh\phi z$$

$C_A = C_{As}$

$z = L$

$\frac{dC_A}{dz} = 0$ $\quad z = 0$

So, you have the equation now, d 2 C A. If I define it d 2 C A by d Z square minus phi square C A is equal to 0 where phi as I defined that is basically, in terms of the Thiele modulus right. So, phi which is under root of m by D that is; in terms of this K by D. L n into K by D but define in this form so, sometime we write it m into L also right, where m is square root of K by D.

So, if you have this information so, the solution of this kind of differential equation is simply in the form of either hyperbolic function or in the form of C A is equal to just if I write it A 1 e to the power m L or phi right so, I will write it m Z or phi Z. Now, phi Z A 2 e to the power minus phi Z; so, A1 e to the power phi Z plus A 2 e to the power minus phi Z or in the form of hyperbolic function one can write A cos hyperbolic phi Z. So, A cos hyperbolic phi Z plus B sine hyperbolic phi Z. A kind of differential equation solution of these you must have read in mathematics course right.

So, what are the boundary conditions to find out a and b that can be find out so what is the boundary condition in this case for straight cylindrical pore? Z is equal to 0 C A is equal to C A S right. Because at the pore mouth the concentration is known to you and at Z is equal to L this gradient of concentration because nothing can diffuse out if the pore is closed from one end. So, this is the pore which is closed from the end so, Z is equal to L, d C A by d Z is equal to 0 right. So, these boundary conditions can be solved and you have the concentration in the pore or you can solve this equation for C A by C A S right. That is; the concentration profile which will be a function of Thiele modulus right.

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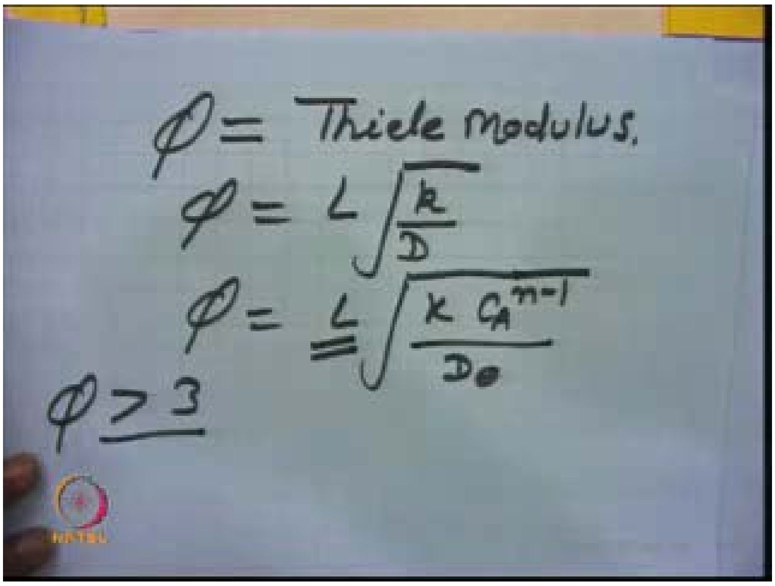

ϕ = Thiele modulus.

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

$$\phi = \underline{\underline{L}}\sqrt{\frac{K\,C_A^{n-1}}{D_e}}$$

$$\underline{\phi \geq 3}$$

So, this phi which is important property of a catalyst or just to check whether diffusion is controlling or not this is known as Thiele modulus right. And, for any first order reaction phi is defined by L under root of K by D. For any n through order reaction phi is defined by L under root of K or C A to the power n minus 1 upon D e like this right. So, one can say generally high value of phi because it is related to your size of the pore right that is; one dimension characteristic dimension we call basically, later on for palette we talk v p upon s x based on the volume of the particle divide by surface area. But here, we are defining it based on the pore single pore so, it is length of the pore right. So, it is length of the pore right k is the kinetic rate constant based on volumetric unit C A n is the concentration at the surface and d is the effective ((Refer Time: 30:09)).

So, most important parameter here, is the size of the pellet right and, the rate constant K right. So, it means; generally phi is greater than 3 in this case then we say diffusion is the rate controlling right. Because this value of phi gives you the idea whether diffusion is rate controlling or this kinetics is rate controlling. Generally, right now just I have done and not solved the equation. So, basically what is you have to do that C A by C S find out the concentration profile by solving this equation you can very easily solve this equation right.

So, C A by C A S and then, you will get a concentration profile. And, then you have to find out the effectness factor which I am not covering right now, I will talk little later before I want to go for this spherical pellet. So, first thing that the solution of this equation which is based on this 2 boundary conditions so, one can very easily find out the latency between C A by C A S concentration profile right.

Because this is; the first equations suppose if I use this equation that Z is equal to 0 right, A to the power phi Z plus A tau phi Z right. So, put your Z is equal to 0 C A is equal to C A. So, one equation you will get from here, which is simply this is one, this is one. The A 1 plus A 2 is one right and second Z is equal to L, d C A by d Z is 0. So, this will become differentiation of this right.

So, just first calculate d C A by d Z. So, that will be phi to the power phi Z here. And, same thing minus this thing right and you have Z is equal to L so this will come in the form of L. So, solve these equations for C A by C A S so, basically it will come in the form of e to the power of phi L to the e to the power of phi L divide by 2 if you solve that so that is to be done right.

So, I will do that later but before that so, once you know that these things that is; for the straight cylindrical pore how to get the differential equation? And, get the concentration profile in a pore? So, one thing is clear that when the diffusion resistance is strong then your concentration will drop faster right. Because depending on the pore size that is; the characteristics of the pore and the size of the pellet if you talk a pallet then there will be a kind of gradient inside the pore.

Now, let us; look at here the same equation that is when we look at in this case spherical pellet now, so the approach is same just for because that was the simplest case for a straight cylindrical pore we discuss that. Now, in this case when you look at this is spherical pellet having some radius porous material right. So, a pellet this is spherical pellet with some radius r and r plus delta r the material balance will be written right, a total radius of the pore pellet is R. So, here it was a pore and here, we are talking non-spherical pellet diffusion through a spherical pellet but equation will remain same. So, this equation which is written here is basically, your 4 pi r square.

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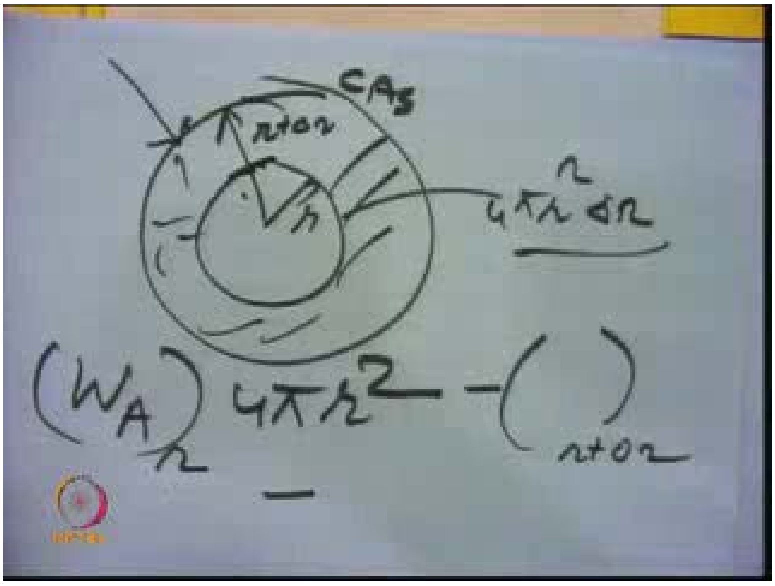

Because now, in this case basically, the diffusion is inward right because the gas species will come here and diffuse. So, actually the input is at r plus delta r if I just take a differential shell having a radius r and r plus delta r in a total spherical pellet. So, basically this is r plus delta r. So, input is there as r plus delta r and output is at r right. But by convention we can just say that the input is still at r but with negative sign and flux is negative here and same thing at r plus delta right.

So, means one can write the differential equation either saying input here minus output here or one can still say that the flux is in the negative side of that r. As r is increasing this side but the flux is in the direction of negative r decreasing r right. Because the concentration highest is here C A S at the surface and then it is decreasing. So, in this case again the equation will remain same only thing that W A r which is the flux at any radius r. When I am saying now, in here and defined by the same expression of fixed log diffusion minus D e d C A by d Z here right.

But area which is the most spherical cell right. So, area normal to that plain so, that will be now, 4 pi r square instead of pi r square which was the cross section area in a cylindrical pore now, this is; 4 pi r square. So, that expression will be W A r into 4 pi r square minus the same thing at r plus delta r right and minus this ((Refer Time: 35:07)) because of chemical reaction. So, there we have defined it based on the area of the pore right. Here is the solid mass, solid pellet so, it is better to define it based on the mass of a catalyst.

So, that is the 3 term that has been written how the second term which is shown here is r A dash. So r A dash is the rate of reaction per unit mass of the catalyst. So, mass of the catalyst has to be multiplied by the mass of that differential section so, this is; a differential section of the cell having radius r and r plus delta r right. So, the volume will be 4 by 3 pi r cube at the r into density. And, the outer section will have 4 by 3 pi r plus delta r whole cube and to their density.

So, the mass of the differential selection will be the difference of these or in other words if you solve it will become 4 pi r square delta that is; the volume of that differential cell So, volume of this differential cell is simply 4 pi r square into delta r that is; simply you subtract that 4 by 3 pi r plus delta r square whole cube minus 4 by 3 pi r cube and multiplied it by density. So, cell volume is 4 pi r square delta r multiplied by the density. So, this is the basically, into 4 pi r square here. And, then is equal to 0; so, that 4 pi r square has been cancelled 4 pi has been cancelled from this side. So, finally, only that directly the differential equation has been shown here right.

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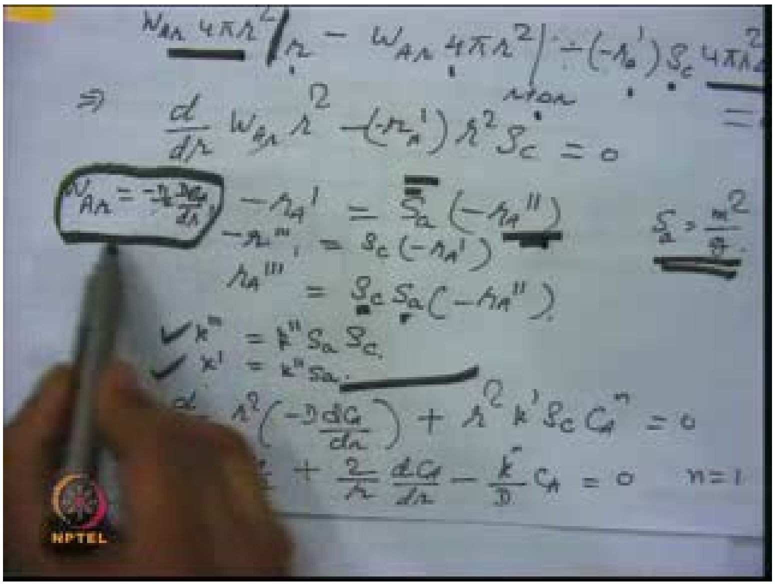

$$W_{Ar} 4\pi r^2\Big|_r - W_{Ar} 4\pi r^2\Big|_{r+\Delta r} - (-r_A')\rho_c 4\pi r^2$$

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

$$\boxed{W_{Ar} = -D_e \frac{dC_A}{dr}} \quad -r_A' = S_a(-r_A'') \qquad S_a = \frac{m^2}{g}$$

$$-r_A''' = \rho_c(-r_A')$$

$$r_A''' = \rho_c S_a(-r_A'')$$

$$✓\ k''' = k'' S_a \rho_c$$

$$✓\ k' = k'' S_a$$

$$\frac{d}{dr} r^2\left(-D\frac{dC_A}{dr}\right) + r^2 k' \rho_c C_A^n = 0$$

$$+ \frac{2}{r}\frac{dC_A}{dr} - \frac{k}{D} C_A = 0 \qquad n=1$$

So, if you look at the exact which I have made it separately for understanding that W A r into 4 pi r square evaluated at r minus W A r which is the flux W A r is minus D e D C by D r 4 pi r square evaluated at r plus delta r minus disappearance mass of the catalyst. So, minus r A dash times the density of the catalyst right O C and multiplied by the volume of the shell right. And, when you divide it by 4 pi r square and take the limit delta r to 0.

So, your equation now, becomes d over d r of W A r into r square minus r A dash into r square O C is equal to 0 which is the equation shown here right. So, W A r all of you know is given by fixed log diffusion so this one is your minus D e D C A by d r. And, rate of reaction now, has been defined per unit mass of the catalyst but I have already told you that, rate of reaction per unit mass of the catalyst, multiplied by mass of catalyst will be equal to rate of reaction per unit area surface of the catalyst multiplied by the surface area of the catalyst which is De t surface area. And, that is also equal to rate of reaction per unit volume of the catalyst multiplied by the volume of the catalyst.

So, this is what shown here is minus r A dash which is equal to per unit mass of the catalyst can be written in terms of because this is surface area per unit mass B e t surface area right. When you report B e t surface area you write meter square per gram right or in one way I can write here, r A dash into mass of the catalyst is equal to r A double dash into total surface area of the catalyst without any mass unit right. So, mass has gone here, so this is; your per unit mass data. And, that multiplied by the rate of reaction per unit surface area so, either unit can be used as I discussed before also if you write it based on volume unit. So, minus r A triple dash is equal to because now, mass divide by the volume of the pellet per unit volume of the catalyst pellet. So, that will become density of the catalyst pellet and times the minus r A dash. So, this is the relation between r A triple dash and r A dash. And, if you just now; combine these 2 you can very easily write r A triple dash which is equal to O C times S a and times minus r A double dash right.

So, one can very easily write down a relationship among 3. And, either when you write either in terms of weight or you define in terms of rate constant no change right. So, k triple dash is again equal to k double dash times S a times O C. And, here k dash is k double dash times S a; so, one can very easily co-relate the k triple dash k double dash and k dash right.

So, that is what written here, and once you have the idea about that now, this differential equation which is in the flux fixed log diffusion substitute it here in the form of W A r which is shown here right. So, W A r is minus D e D A by d r; one can write it in the form of mole fraction also, y A is mole fraction. So, C total concentration into mole fraction is your C A molar concentration. So, by using this if you substitute so, your equation comes out to be minus d r over D e of minus d C A by d r times r square minus the same term r a dash O C into r square is equal to 0 right.

So, this is the formulation of differential equation for a spherical pellet. Similarly, one can write the differential equation for a cylindrical pellet also initially I have shown for a pore in the case of cylindrical pellet it will be now, length of the cylinder right. And, 2 pi r L that is; the approach will be similar what you have seen earlier right for a cylindrical pellet and the diffusion is taking place along the length right.

So, here the finally, a formation of differential equation which is d over d r of r square minus D d C A by d r plus r square k dash O C and C A to the power m for any because we have to find out what is r A dash? So, it can be your first order rate, it can be second order, it can be nth order also. So, that is the equation for n th order. So, in simplification if you do so, d 2 C A by d r square plus 2 upon d C A by d r minus k by D C A is equal to 0 for first order reaction. So, how did you get this? Just now, simplify this equation right. So, d over d r of r A square D by d C d r. So, first one is the differentiation of the other one r d C by d r and this diffusion co-efficient is a constant.

So, first thing is that this has been taken to this side right. So, diffusion co-efficient is k by we have just taken divided by D. But you cannot take this r square out make it clear right. Because this in inside the differentiation equation so, d over d r of r square d C by d r. So, d over d r of first thing is d 2 r square will be out so, it will become d 2 c a by d r square right. Second time it will become your differentiation of this that will be 2 r right now, you can divide by r square.

So, then it has been divided by r square so, it will become d 2 C A by d r square plus 2 upon r d C A by d r minus k by D because this r square consists. Now, so k by D times O C time C A is equal to 0 by k dash O C I have shown you that k dash times O C can be written in the form of k triple dash volumetric rate constant which can be written based on these 3 right. So, the choice is yours one can write in the form of the same expression k dash times O C or you write k dash times O C which is written here in terms of this. So, that has been written in terms of volumetric rate constant and just for simplification. Because most of the time the rate will be defined per unit mass of the catalyst.

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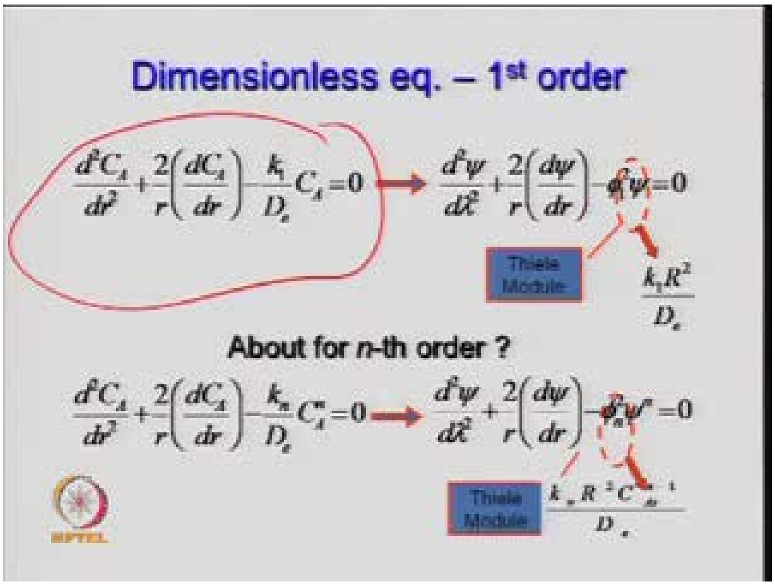

Dimensionless eq. – 1st order

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

Thiele Module

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

About for n-th order ?

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

Thiele Module

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

So, once this is known, you need a boundary condition. So, this is what the equation which has been written here first and equation need to be solved. So, there are numerical methods which are available nowadays, rather one can go with the analytical technique also very briefly we will talk on that. But it is advisable for this kind of differential equation. And, to have a concentration profile right rather having a final value of the concentration, which you get in the analytical approach it is advisable to go with the numerical techniques right. And, the solutions or methods are available in many software tools polymers met lab as I discussed earlier right. So, here the important thing what I said is the boundary condition first.

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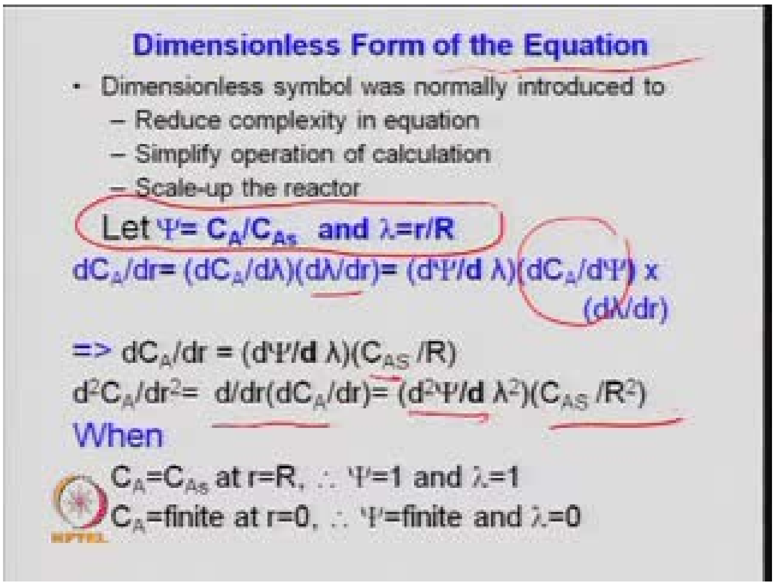

Dimensionless Form of the Equation

- Dimensionless symbol was normally introduced to
  - Reduce complexity in equation
  - Simplify operation of calculation
  - Scale-up the reactor

Let $\Psi = C_A/C_{As}$ and $\lambda = r/R$

$dC_A/dr = (dC_A/d\lambda)(d\lambda/dr) = (d\Psi/d\lambda)(dC_A/d\Psi) \times (d\lambda/dr)$

$\Rightarrow dC_A/dr = (d\Psi/d\lambda)(C_{AS}/R)$

$d^2C_A/dr^2 = d/dr(dC_A/dr) = (d^2\Psi/d\lambda^2)(C_{AS}/R^2)$

When

$C_A = C_{As}$ at $r = R$, $\therefore \Psi = 1$ and $\lambda = 1$

$C_A =$ finite at $r = 0$, $\therefore \Psi =$ finite and $\lambda = 0$

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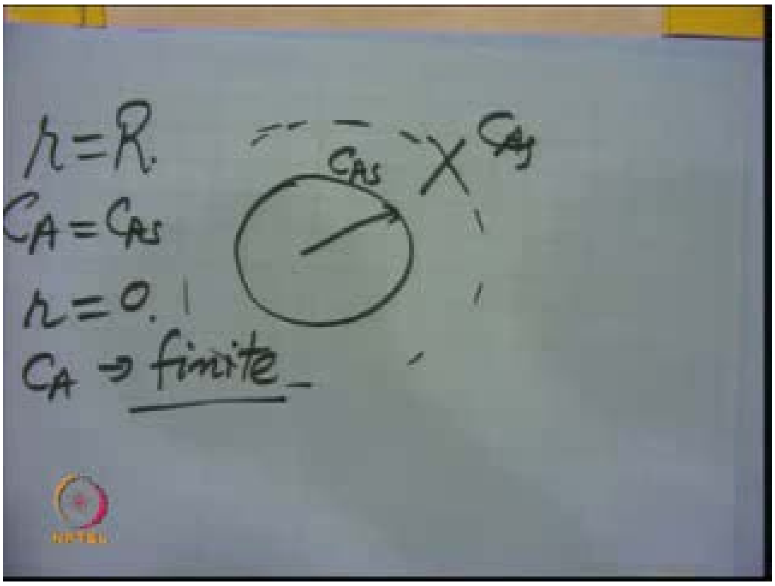

So, I think before going this let us, talk on the boundary condition right. Boundary condition; so, you know a spherical pellet something like this; and at the surface the concentration is known right. If I just say that this is a spherical pellet and this is your concentration there is a film basically if you look at the external mass transfer also. But we have already said that this is not controlling so, then it can be this is C A g and this is not controlling this will be C A g known concentration right or in general we write it some known concentration C A S. So, r is equal to R the first boundary condition your concentration is known. So, C A is equal to C A S right that is; the first one. And, r is equal to 0 that is; center of the pellet C A cannot be 0.

What we will use one can use d C A by d r 0 right. Because of symmetry also but the important here that r is 0 at the center the C A will have some value it is finite it cannot be infinite because down the length the concentration of the reactant species is different right. So, it means it will decrease with radius inside if you move towards, because diffusion is from outer surface to the inner surface for the reactant species right. So, this is the first thing that boundary condition second is that why do we need some kind of dimensions parameters right?

So, we need the dimensionless because this kind of equation can be solved better and interpreted better for the commercial success. And, we need to find out the dimensionless equations right. So, these are the called because it reduces the complexity of the equation the number of variable can be reduced by heating this also right. Simplify operation of calculation and scale-up becomes easy that is; the we define some dimensionless parameters. And, based on that we solve the equations now, we have and equation of this form.

So, this equation d 2 C by d r square plus 2 upon r d C A by d r minus k A by D e times C A is equal to 0 for spherical pellet one need to solve this equation right. The equation can be solved analytically also. But preference will be given to the numerical technique. So, in this case we are using some dimensionless variable this side. So, define some parameters like psi. So, psi is a dimensionless concentration defined by C A by C A S right. And, Lambda is another dimensionless length defined as r by R right so that is any radius r divided by the total radius of the pellet which is known to you right.

So, it means the dimensionless equation psi and Lambda. So, this equation can be represented in form of a dimensionless form like this right. Now, instead of you saying want 0.5 m radius of the pellet or 5 m radius of the pellet. You can just talk in terms of the position right that is; r by r 0.2 r by r 0.5 r by r 1 like that, now, irrespective of the dimension of the pellet right. So, 1 means you have 1m m pellet or 10 m m pellet. When you look at in a lab scale reactor it is a powder of 100 micron. But when you look at a commercial pellet scale it can be 1 m m or 1.5 m m right. So, you need not to bother about that same thing in terms of the concentration radiant.

So, you may start with 10kilo mole per meter cube right or you may start with just 1 in terms of the 0.05grams mole per meter cube any choice of the concentration can be used. Because we are talking now, in terms of C A by C A S right. That is what is the concentration at the surface or initial concentration. And, now how much is left? Because rest is reacted so, that is important here, in this case. So, we can use this dimensionless variables and I hope all of you know this part how to write the equation? So, quickly I have written here in terms of inter conversion right.

So, this d C A by d r we have to find first right. So, d C A by d r can be spited based on chain rule of partial differentiation right. So, that is; simply, d C A by d Lambda into d Lambda by d r. So, that is; what d C A is to be written in terms of the psi and Lambda is r is to be written in the form of Lambda. So, first thing has been done that this r has been replaced in the form of Lambda. So, d C A by d Lambda into d Lambda by d r. So d Lambda by d r one can calculate from here right.

So, d Lambda by d r is simply 1 by r and d C A by d Lambda now, you can split it in the form of psi so, that becomes d psi by d Lambda right and times d C A by d psi. So, basically it is d C A by d psi times d psi by d Lambda and d C A by d psi one can calculate from here. And, if you look at here so, multiply it by the 3 term which is already there d Lambda by d r right. So, if you do that so, just for understanding I have written here so, d C A by d r. Now, becomes your d psi by d Lambda now, we have changed that in this form and differentiation of this d C A by d psi that is equal to C A S right. From this equation and which is written here, and the 2 term is d Lambda by d r differentiation of this is 1 by r.

So, that means d C A by d r has been replaced by d psi by d Lambda times C A S by R. Why we are doing this, I will let you know right because the reason is that we want to simplify our differential equation for analytical solution right. Otherwise one can solve the equation by finite difference method also using the numerical techniques right. So, similarly, one can write d 2 C A by d r square also, d 2 d A by d r square is simply equal to d over d r of d C A by d r you know that right and, d C A by d r we have already done right here.

So, that will simply now, d over d r is to be replaced in this form what you had done earlier. So, overall what you have d psi by d Lambda which is here. So, differentiation of that because d over d Lambda into d Lambda by d r right. So, that I d 2 psi by d Lambda square which is from here, this differentiation of this is with respect to Lambda. And, again you have d Lambda by d r so that will be 1 by R. So, this is C A S upon R square right. Very simple how to chain the equation in that is; dimensionless form of the variables of that what we have done here.

Boundary conditions you know now, because initially its C A is equal to C A S and r is equal to R. Now, it will become psi is equal to 1, at lambda is equal to 1 right. And, second C A is finite, at r is equal to 0, now psi will be finite, and at lambda is equal to 0. So, when you do that, you will have the same term right. So, the equation now, which is in this form which we have discussed here, has been now written like this right.

So, that is; what the term if you look at d 2 C A by d r square we have substituted d C A by d r we have already defined in terms of this will be chain to d psi by d Lambda square that has changed to d psi by d Lambda basically here it is not r right. So, that is again here in this form and K A by D e times C A. So, that has got the term in the form of r square which is shown here, all these terms together C A S times R square which is a constant right so, radius of the pellet and surface concentration.

So, based on this the equation has been simplified to this form. So, pi square which is other than all the term which is psi and that has been considered as a psi square ((Refer Time: 52:48)) modular. What I defined earlier right I will come back again for details of the psi square later. But at this stage this number which has arisen in writing the equation it is simply here, K 1 times R square divide it by D e right.

So, r under root k by d is your psi where R is the radius of the spherical pellet right. And, if it is; nth order reaction then this will be written like K for nth order reaction divided by D e times C A S to the power n. And, that time this psi will be r is r under root of K C A to the power n minus 1 divide by D e which I had already discussed right. So, basically for first order reaction psi is r under root K by D. And, for any nth order reaction psi is r under root of K C A S to the power n minus 1divided by D e right.

So, we will come back to that point again because this is very important when you look at a heterogeneous catalytic reaction. The diffusion resistance is very important phenomenon that comes because of the pore size, pore size distribution and pore radius, pellet size right, And, one needs to remove them the resistance is which is because of the diffusion that has to be eliminated once you want to study the kinetics of the ((Refer Time: 54:05)) right.

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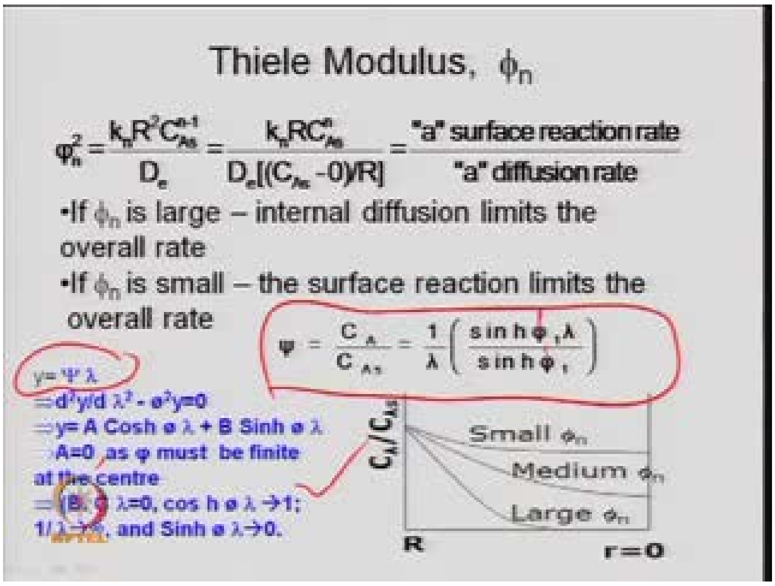

Thiele Modulus, ϕ_n

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

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

$$\psi = \frac{C_A}{C_{As}} = \frac{1}{\lambda}\left(\frac{\sinh\phi_1\lambda}{\sinh\phi_1}\right)$$

$y = \Psi\lambda$

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

$\Rightarrow y = A\cosh\phi\lambda + B\sinh\phi\lambda$

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

$\Rightarrow$ (B.C) $\lambda=0$, $\cosh\phi\lambda \rightarrow 1$; $1/\lambda \rightarrow \infty$, and $\sinh\phi\lambda \rightarrow 0$.

So, the solution of this kind of equation is possible analytically just by assuming some parameter in which relates this y psi and Lambda together otherwise, it becomes difficult to do analytically but or one can solve it through Basels function right. So, Basels function of different orders one can use here and solve them right. But the computational methods are better nowadays, and this is one analytical method by which you can solve it right. So, just if you define a parameter another parameter which can combine psi and Lambda in 1equation right. So, we have defined y is equal to psi into Lambda.

So, it means your d 2 y by d Lambda square right, you can write differentiation of this of that equation and which we have already written earlier here. So, if you just substitute that the terms get cancelled right. Because we are substituting there are now, d 2 psi by d Lambda square and d psi by d Lambda. So, that second term will get cancel when you substitute this term. And, just for your exercise one can do that right that just so understanding one should do that.

So, I have written it quickly that if you write y is equal to psi into Lambda then the equation which is written in the original from here, in this form this equation has now, been simplified to this form d 2 y by d Lambda square minus pi square y. And, this equation just I was talking when I was discussing the diffusion in the pore similar equation here right. And, solution of this kind of equation is very standard right that is; y is equal to a cos hyperbolic pi Lambda plus b sign hyperbolic pi lambda either you write in this hyperbolic functions form or you write it in the form of exponential right. C 1 A to the power pi Lambda plus C 2 into the power minus pi Lambda right.

So, either exponential power or this both terms can be used here. And, boundary condition I told that at center of the pellet it has to be finite, concentration has to be finite. And, at the outer surface that is; the C A by C A S was 1 right that is; what we have already defined. So, if you use that A is equal to 0, A will has to be 0 rather this because at the center of the pellet that is; Lambda is equal to 0 or your cos hyperbolic phi Lambda if you calculate right. So, what I will do y is equal to psi Lambda you have to interoperate it like this y is equal to psi Lambda which is a cos hyperbolic pi Lambda plus B sin hyperbolic Lambda.

So, your psi is equal to A by Lambda times this plus B by Lambda times this right. So, when Lambda is 0 you are saying so, this is; indeterminate form so you need to solve. So, cos hyperbolic pi Lambda because when lambda is 0 cos hyperbolic this lambda test 0 I should say. Then cos hyperbolic pi Lambda becomes 1 right and sin hyperbolic term become 0. So, this says that because Lambda is in the denominator right also. So, it means; there are this psi has to be infinite, concentration has to be infinite which is not possible. So, it means your constant A has to be0 this is the interpretation based on this boundary condition.

So, once A is 0 then your simply your y is equal to B sin hyperbolic pi Lambda right. So, psi is equal to 1 upon Lambda B sin hyperbolic phi Lambda used by second, first boundary condition that you know that at r is equal to R, C A is equal to C A S. So, use that and find out the constant and you can solve that equation. And, that is what written here; so, psi is equal C A which is defined as C A by C A S is 1 by Lambda sin hyperbolic pi Lambda which is Thiele modulus divided by sin hyperbolic pi Lambda.

So, this is basically Thiele modulus here right. And, same expression because that time I have not shown you same expression will be used, will come for the pellet also, C A by C A S is equal to sin hyperbolic pi L there divide by sin hyperbolic y right. And, that term will be living there that is; 1 upon L b q is defined. So, I will continue it next time so, I stop here today.

Thank you.