Chemical Reaction Engineering 2 (Heterogeneous Reactors)
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Lecture 08
Shrinking core model continued for type D reactions

Ya we have completed the shrinking core model, I think except Rinita others were not there so you have to take notes from her and we have also discussed the extreme conditions like which are rate controlling, how do you find out the mechanism, which one is rate controlling all that we have discussed so based on that now I would like to go you an assignment. So I will give you the parameters you have to plot these assignment which is graphical but each graph atleast you should be able to write on that graph atleast 10 to 15 sentences, it is not simply go to XL and then plot and then give it, okay so that anyone can do whoever knows the computer programming but what your expertise comes there is that if you are able to predict why something is increasing, something is decreasing, something is not increasing, decreasing all that you know physical phenomena, right.

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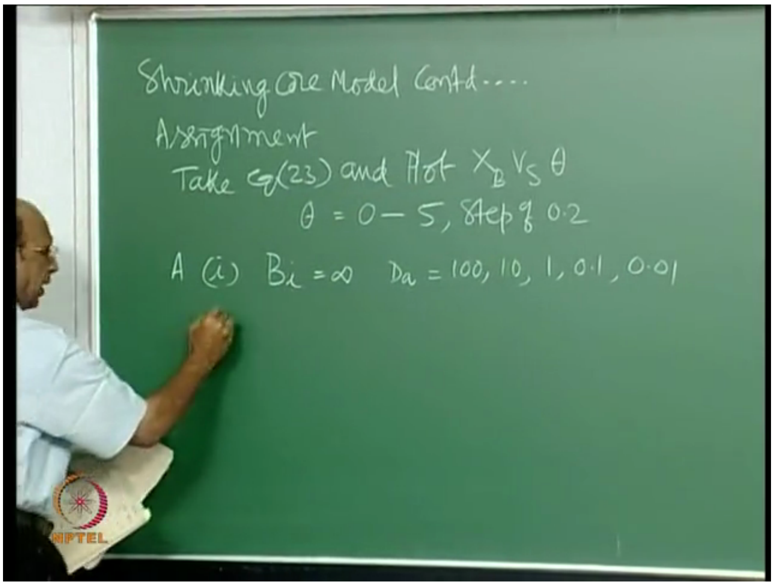
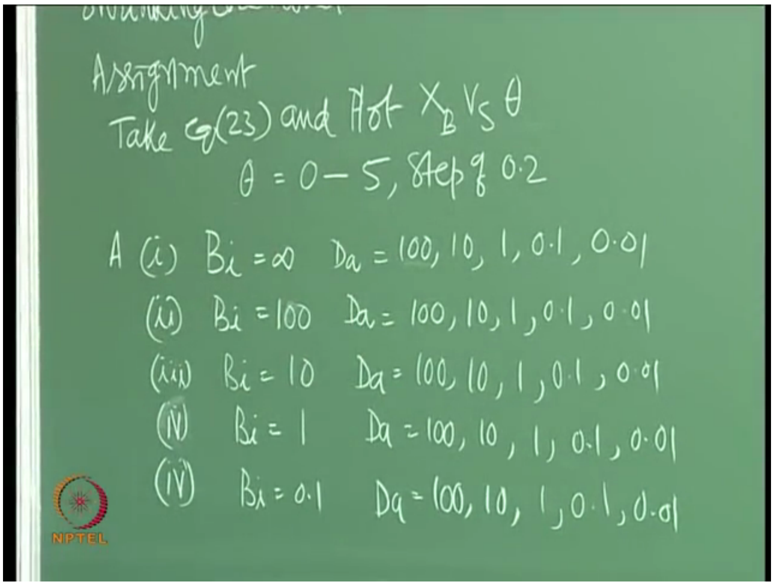


Shrinking core Model Contd....
Assignment
Take eq(23) and Plot X_B vs θ
$\theta = 0 - 5$, step of 0.2
A (i) $B_i = \infty$ $D_a = 100, 10, 1, 0.1, 0.01$



Assignment

Take Eq(23) and Plot X_B Vs θ

$\theta = 0 - 5$, Step of 0.2

A (i) $Bi = \infty$ $Da = 100, 10, 1, 0.1, 0.01$

(ii) $Bi = 100$ $Da = 100, 10, 1, 0.1, 0.01$

(iii) $Bi = 10$ $Da = 100, 10, 1, 0.1, 0.01$

(iv) $Bi = 1$ $Da = 100, 10, 1, 0.1, 0.01$

(IV) $Bi = 0.1$ $Da = 100, 10, 1, 0.1, 0.01$

So the assignment is you take for example that equation number dimensionless equation number what is that number 23, or 24? In terms of Biot number and Damkohler number S equation number 23, okay. Take equation 23 and plot X B versus theta, theta is the dimensionless time X B ofcourse will be conversion, okay. So the range for theta will be 0 to 5 in the steps of 0.2, okay that means you know 0.2, 0.4, 0.6, 0.8, 1, 1.2 like that, right okay and X B is ofcourse 0 to 1 anyway that I do not have to tell.

So what we have to do is A 1 Biot number equal to infinity there are two numbers Biot number and Damkohler number so and Damkohler number equal to 100, you have to keep Biot number infinity and change Damkohler number 0.1 and 0.01, so then come to Biot number equal to 100, Damkohler number is same 0.01, then Biot number equal to 10, Damkohler number is very less same ranges 10, 1, 0.1, 0.01, then we have Biot number (oh sorry) Biot number equal to 1, Damkohler number equal to 100, 10, 1, 0.01, then we have the 5th one Biot number equal to 0.1, Damkohler number is same 100, 10, 1, 0.1, 0.01, I think from this you will get almost all the information X B is varying with Biot number in that equation X B is a function of theta, Biot number and Damkohler number that is all no nothing else is there in that all of in the form of dimensionless numbers so then you vary.

And now you have to say that for the comparison when you are plotting these graphs for example if there is a change between this and this why there is change the physical phenomena or if there is no change between this and this why there is no change, what is actually happening and you know very large Damkohler number means which one is controlling? What is the Damkohler number definition? Ya large number means mass transfer diffusion control, diffusion through the Ash layer controlling, okay.

So when diffusion through Ash layer controls then what kind of phenomena, what kind of things are going on within the particle so all that information you have to write, you have to write you know atleast 1, 2 or 3 A4 pages and then attach these graphs and then submit, okay it is upto you, okay if you do not submit then in examination if you are not doing well please do not ask me, right ya for the people who want to definitely pass I think it is very difficult and I do not consider at all if you are not doing all this, this is only for your help I may give the same thing in the examination, okay at that time this is a practise.

And the physics if you understand after plotting and after writing then definitely you will understand and do not think you are heroes when you copy, copying is not heroism actually solving and writing is heroism but most of the time you will keep quite till last day and then last night we will just ask someone else assignment copy and give as if you fool me actually you have fooled me you fooled yourself first without doing.

So that is why these assignments even though there are marks I think you cannot only measure everything in terms of marks, you do not learn anything, if you do really that, okay.

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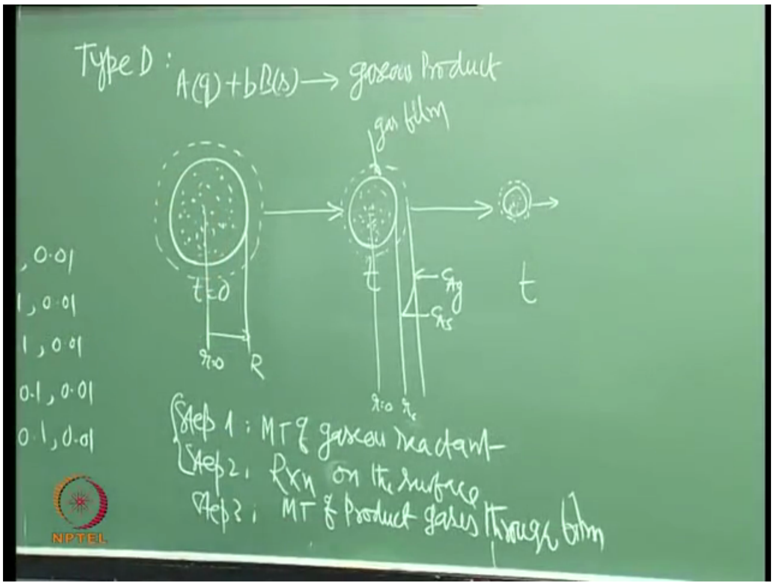

So after this what we have to do is one other type reaction type D reaction if you have notes can you tell me what is type D reaction? We will derive an equation for type D reaction ya so this will be A gas plus bB solid going to gaseous products, right ya what is the example gaseous product ya combustion, gasification there are very nice reactions where at the end you will not see any particle, everything will be disappearing.

So that is the one for that kind of reactions now we have to develop a shrinking core model, right what is the difference? What could be the difference? (())(7:41) diffusion will not be there, okay because every time the particle outer layer is first converted then slowly it moves and there is no because everything is becoming gas and coming out there is no solid product so that is why.

And how we derive that we will see and before that let us imagine our particle how it is moving this is particle at time t equal to 0 may be coal particle so then after sometime t then we will have this is the size then after sometime t this is the one and finally disappears do nothing okay ya so now this is t sometime t ya okay good. So what is the difference is at time t equal to 0 just when you have the reaction started t 0 plus for example that is the film, then this is the film, then you will have this (())(9:04) gas film, right.

It must be very easy for us now to derive this because there is no one more resistance, there is no ash forming so there is no diffusion and if you are able to plot the profiles this is r equal to 0 (())(9:38) and this is at any time I will call it as r c and here we call this one as capital R that is initially at time t equal to 0, then only the core is the particle is shrinking overall but I am trying to maintain the same notation r c is the diameter of the core which is shrinking but the overall particle itself is core for us not like in the other case where inside the particle you have a core unreacted core which is shrinking but here the entire particle is shrinking.

So as usual if I draw the profile like that that is all this is C As when it touches the surface then reaction is taking place and particle is slowly disappearing because everything is becoming gas gaseous product so you will have this kind of situation at after sometime t, good.

So what are the steps now we have step 1 is mass transfer MT of go to abbreviations of gaseous product sorry MT of gaseous mass transfer of gaseous reactant. Step 2 is reaction on the surface reaction on the surface, is there step 3? No, why no? Ya see the gaseous products have to come through the film again, right ya they have to ya but we do not take that one step 3 equal to MT of product gases product gases through film but it does not matter for us because it is not reversible reaction so that is why okay.

So that is why only these two steps you have to take and at steady state mass transfer of reactant A going through the film must be equal to rate of reaction on the surface so that we know we already are masters of that.

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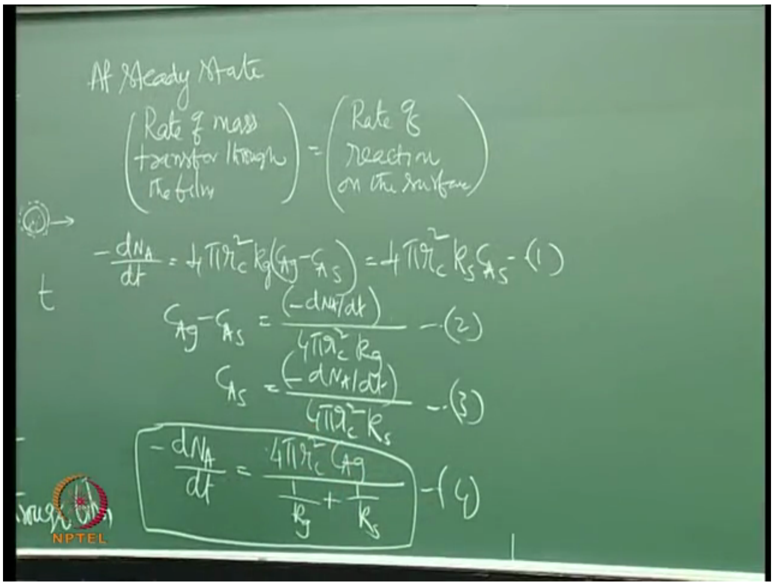

At Steady State

$$\begin{pmatrix}\text{Rate of mass}\\ \text{transfer through}\\ \text{the film}\end{pmatrix} = \begin{pmatrix}\text{Rate of}\\ \text{reaction}\\ \text{on the surface}\end{pmatrix}$$

$$-\frac{dN_A}{dt} = 4\pi r_c^2 k_g (C_{Ag} - C_{As}) = 4\pi r_c^2 k_s C_{As} \quad -(1)$$

$$C_{Ag} - C_{As} = \frac{(-dN_A/dt)}{4\pi r_c^2 k_g} \quad --(2)$$

$$C_{As} = \frac{(-dN_A/dt)}{4\pi r_c^2 k_s} \quad --(3)$$

$$\boxed{-\frac{dN_A}{dt} = \frac{4\pi r_c^2 C_{Ag}}{\frac{1}{k_g} + \frac{1}{k_s}}} \quad -(4)$$

So then at steady state rate of mass mass transfer through the film equal to rate of reaction on the surface correct ya. So we know the equations now so this will be minus dN A by dt if I write in terms of equations this is simply rate 4 pi r c square okay and that is the area and mass transfer equation this is k g C Ag minus C As equal to if I assume first order reaction then this will be 4 reaction is on the surface every time 4 pi r c square ok ya so 4 pi r c square k s C As, okay so this is equation 1.

So now ofcourse we have to eliminate this I think I will write that just slightly different way so that some of you can get what is going on. So this is if I write like this this will be minus dN A by dt divided by all this 4 (pi r square) pi r c square k g this is equation 2, okay you have to remember that C Ac also equal to C As so I think let me write atleast once, okay then you are comfortable no problem ya it is on the core but now for us core itself on the is the outer surface, okay good so let me write this one also.

Ya so now C As equal to again minus dN A by dt divided by 4 pi r c square k s correct ya so from these two equations from equation 2 and 3 what we can do is minus dN A by dt equal to 4 pi r c square C Ag divided by 1 by k g plus 1 by k s so this is equation 4 so this is our rate equation but ofcourse if we want to make this one as intrinsic rate so then I have to divide by some area or volume of the particle or weight of the particle whatever, okay so 4 pi r square that means I have just added these two and then separated again dN A by dt that is all very simple, okay.

So now there is a problem here I cannot directly integrate and ofcourse you have another thing here our normal procedure is this equation just gives me what is the concentration profile or how the rate of reaction is taking place with respect to gaseous A it is dN A by dt, right dN A by dt but what we would like to have is also dN B by dt how the particle is shrinking, how the particle finally disappears? So that is what what we have to relate.

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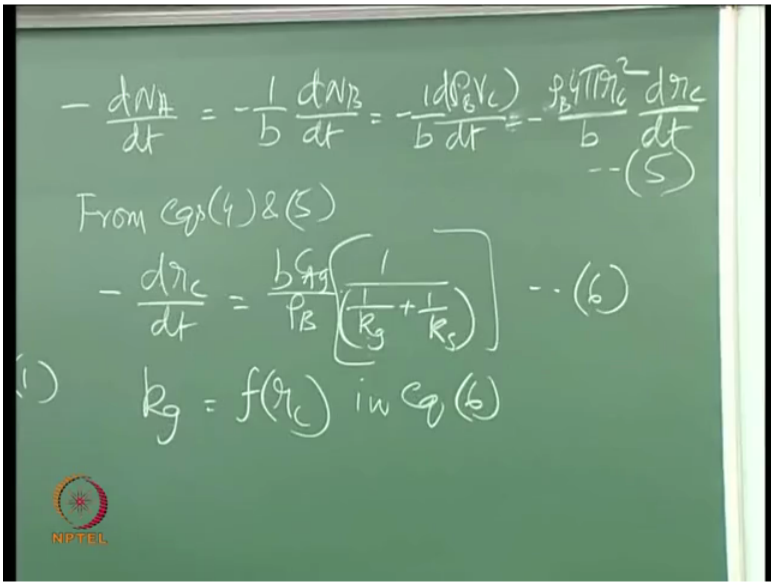


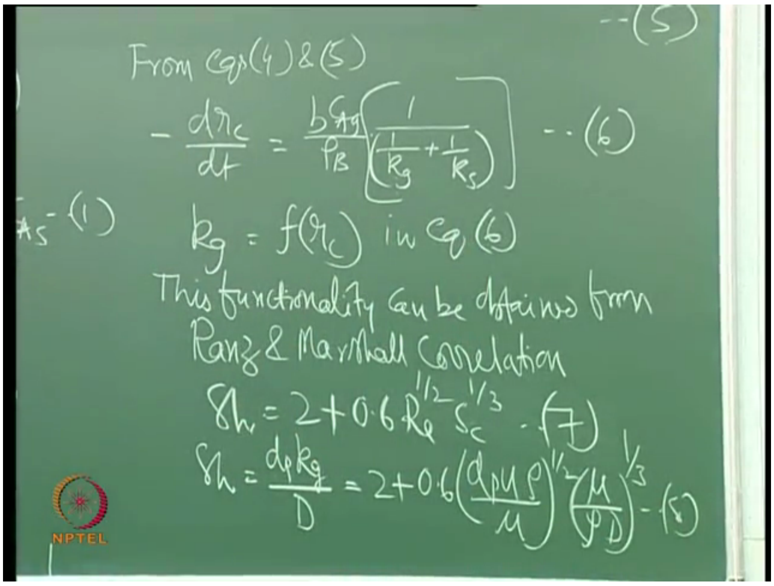
$$-\frac{dN_A}{dt} = -\frac{1}{b}\frac{dN_B}{dt} = -\frac{1}{b}\frac{d(\rho_B V_c)}{dt} = -\frac{\rho_B 4\pi r_c^2}{b}\frac{dr_c}{dt} \quad --(5)$$

From eqs (4) & (5)

$$-\frac{dr_c}{dt} = \frac{b C_{Ag}}{\rho_B}\left[\frac{1}{\left(\frac{1}{k_g}+\frac{1}{k_s}\right)}\right] \quad \cdot\cdot(6)$$

(1)

$k_g = f(r_c)$ in eq (6)



--(5)

From eqs (4) & (5)

$$-\frac{dr_c}{dt} = \frac{b C_{Ag}}{\rho_B}\left[\frac{1}{\left(\frac{1}{k_g}+\frac{1}{k_s}\right)}\right] \quad \cdot\cdot(6)$$

A_s -(1)

$k_g = f(r_c)$ in eq (6)

This functionality can be obtained from Ranz & Marshall Correlation

$$Sh = 2 + 0.6\, Re^{1/2} Sc^{1/3} \quad \cdot(7)$$

$$Sh = \frac{d_p k_g}{D} = 2 + 0.6\left(\frac{d_p u \rho}{\mu}\right)^{1/2}\left(\frac{\mu}{\rho D}\right)^{1/3} \quad -(8)$$

So for that we already that equation minus dN A by dt from this stoichiometry this comes from this stoichiometric equation equal to minus 1 by b dN B by dt which is nothing but minus 1 by b d of once more I will write rho b V c correct dt ya which is again nothing but minus 4 pi r c square by b dr c by dt here also we have rho b ya correct thank you rho b good so this is equation number 5.

Now if I take equation number 4 and 5 dr c by dt can be written as from equations 4 and 5 minus dr c by dt equal to ya can someone quickly tell? Ya b C Ag by rho b into 1 by k g plus 1 by k s so this is the equation which I am supposed to integrate to get the relationship between conversion and time or shrinking core and then time this is equation number 6 ya here only straight forward integration I cannot do, okay why? Because now the procedure is take if there is any r c terms I have to take this side and time I have to take this side and then simply integrate, is there anything which is changing with r c in the other side?

Ya why why it is changing k g changing with r c film (())(18:57) changing ya so film technique changes means what is literary changing, what is changing what is the quantity ya k g, k g is changing with r c, do you have any relationship between k g and r c ya go again to Ranz and Marshal correlation, okay so then we will see small particles or large particles what is the relationship between k g and r c and that relationship we have to substitute here in k g and finally we have to integrate because now this k g is varying with r c that means if you take small particle or large particle you will have I do not know some of you would have done already something in Levenspiel using Levenspiel book in marked analytic reactions, you have done Anurag?

Ya is non-catalytic reactions he gives some very nice conclusions there at the end of the kinetic chapter he has divided that into one is the development of kinetic equations, other one is design two chapters are there of non-catalytic reactions where at the end of the you know kinetic model chapter he he comments that when you have film control the power to the the power to the r to the power of you know t is directly t is proportional to r to the power of 1.5 to 2 it goes many people do not understand. I think now this is one of the best thesis how you can derive that that I do not derive but I will just mention and then give it to you so that I can ask that in the examination, okay.

So t is t time is proportional to r to the power of 1.5 to 2 that means as the particle size is decreasing the exponent falls, okay ya so that you can get from this derivation good okay. Now what we have to write here is k g is a function of r c in equation 6 and you cannot directly derive that I mean integrate that unless you know that functionality, right. So that functionality can be obtained from from Ranz and Marshal Correlation, what is that? Sherwood number equal to 2 plus 0.6 Reynolds to the power of half and Schmidt to the power of 1 by 3 this is equation 7.

The same equation I can also write for me for easy solving this is d p k g divided by D that is diffusivity equal to 2 plus 0.6 Reynolds number it is d p Mu rho by Mu to the power of half and Schmidt number is Mu by rho D whole to the power of 1 by 3 so this is equation 8, okay now we have to solve this okay. Let us see first for small particles for small particles the other term Reynolds number term is neglected small particles means Reynolds number may be very very small. So the centre term may be smaller when compared to 2 one extreme very very small particles, right.

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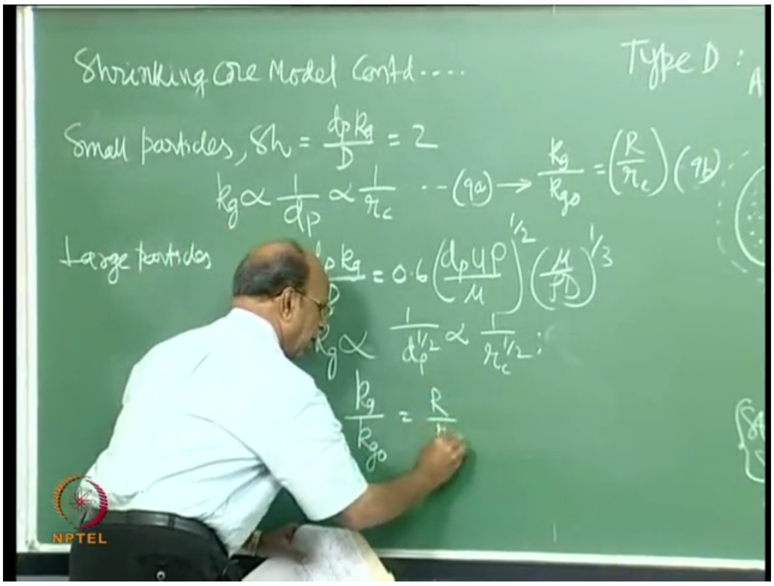

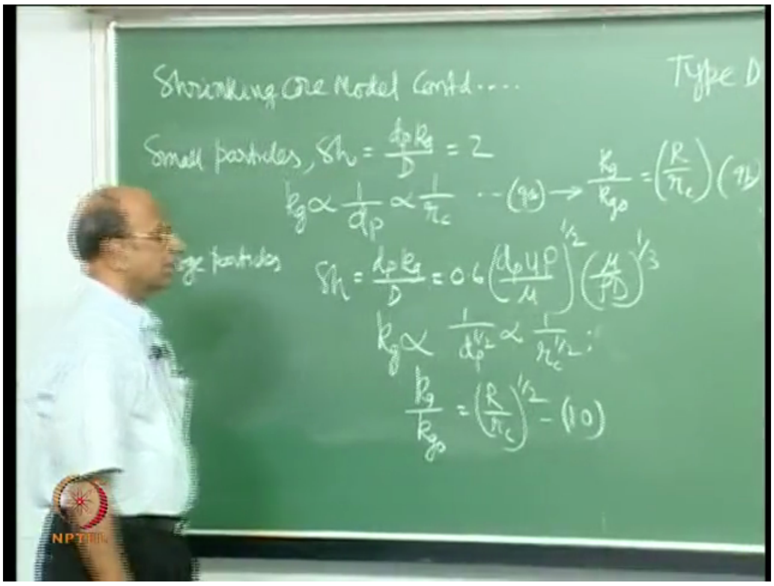

For small particles for small particles Sherwood number equal to 2 which is nothing but again d p k g by D equal to 2 so from this what do you find out k g is proportional to 1 by d p correct no or proportional to 1 by r c radius that is 1 and for large particles this is what is the number 9 this is equation 9 take ya. For large particles Sherwood number okay equal to d p k g by D 0.6 d p Mu rho by Mu to the power of half Mu by rho D to the power of 1 by 3 ya.

Now can you tell what is k g proportional to ya this is 1 by d p to the power of half correct ya also proportional to 1 by r c to the power of half ya good. So if initially our radius equal to capital R right initially then in both the cases initially k g is okay I want to convert this into based on initial particle ya so for small particles I think I may write here for small particles I can write initially k g by k g not equal to k g not I will tell you k g not is the mass transfer coefficient initially, right.

So you will have here R by r c to the power of 1, right initially and similarly here so this is ofcourse also equation 9a, 9b I will write here ya. So here also I can write the same thing k g (I can below also I can write) k g by k g not equal to for large particles ya can someone tell capital R by r c to the power of half, okay. So in general what I can write this may be okay this I will say 10.

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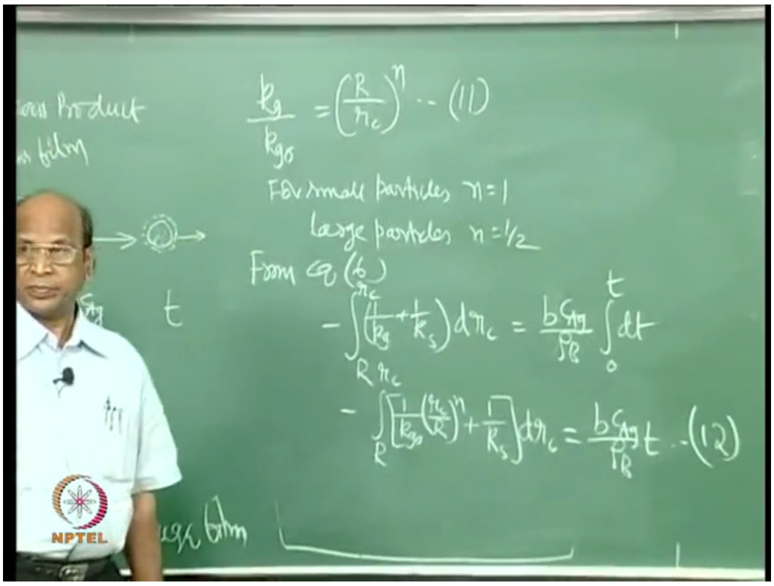

$$\frac{k_g}{k_{g0}} = \left(\frac{R}{r_c}\right)^n \cdots (11)$$

For small particles $n = 1$

large particles $n = 1/2$

From eq (6)

$$-\int_R^{r_c} \left(\frac{1}{k_g} + \frac{1}{k_s}\right) dr_c = \frac{bC_{Ag}}{\rho_B} \int_0^t dt$$

$$-\int_R^{r_c} \left[\frac{1}{k_{g0}}\left(\frac{r_c}{R}\right)^n + \frac{1}{k_s}\right] dr_c = \frac{bC_{Ag}}{\rho_B} t \cdots (12)$$

So in general what I can write is what I can write so in general what I can write is k g by k g not equal to if I take the ratio R by r c to the power of n so this is equation 11 this is equation 11 and we have the two cases if n equal to 1 now the other way for small particles n equal to 1, correct for large particles n equal to half. So I try to integrate this equation using substituting this and then you will have both the cases by substituting for n equal to half you will have large particles and vice versa, there is another important thing also which I have not mentioned to you.

There are some books like Carberry books is slightly Carberry book. So there he also takes u variation with d p or d p variation with u particularly that is correct when you have you know moving bed reactors and also fluidized bed reactors (small) it is reacting becoming smaller so when it is becoming smaller than the terminal velocity ya I think is higher and higher because if particle can be easily thrown out so that variation of u with respect to u how the r c is changing, the relationship between u and r c that also is taken care of.

But here we are assuming that u is constant for us and only d is changing the other things are properties rho and Mu they will not change, right here also diffusivity and all that they will not change only u can be changing and that probably I will give you in the examination some other nice trick there and then I will ask you to do this, okay ya good because everything if I tell you know may not appreciate that, okay.

So now it is only integration that is left now so that means from equation 6 I will simply write from equation 6 minus integral I have 1 by k g plus 1 by k s d r c equal to integral I will take the other things that is b C Ag rho B integral dt this is 0 to t correspondingly 0 means capital R at any time t means r c that is what I have to integrate but I cannot integrate the straight forward because this k g is a function of r c.

So that is why now again minus R to r c here again I will substitute for k g equation 11, so if I substitute that it becomes 1 by k g not into r c by capital n that is one term plus 1 by k s into d r c equal to b C Ag rho B into t, okay ya we also have an equation we also have an equation for r c in terms of X B or X B in terms of r c correct no you know that so what is that equation?

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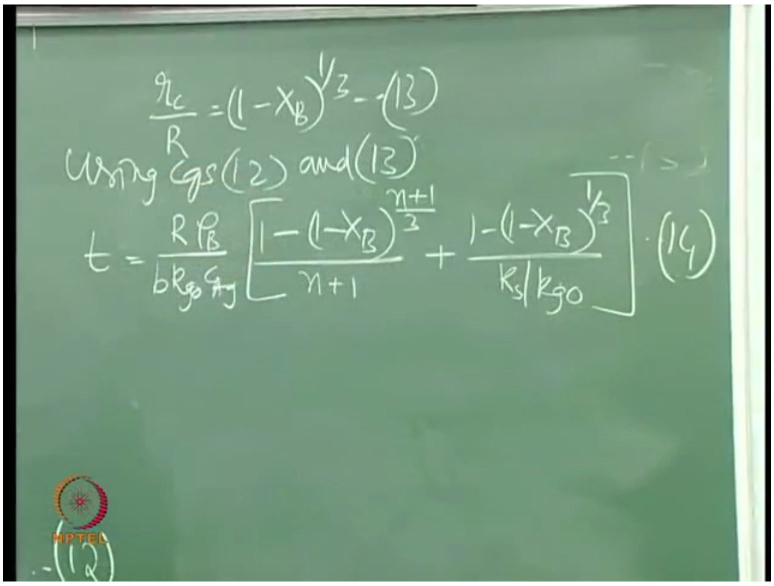

$$\frac{r_c}{R} = (1-X_B)^{1/3} \quad --(13)$$

Using eqs (12) and (13)

$$t = \frac{R\rho_B}{b k_{g0} C_{Ag}} \left[\frac{1-(1-X_B)^{\frac{n+1}{3}}}{n+1} + \frac{1-(1-X_B)^{1/3}}{k_s/k_{g0}} \right] \cdot (14)$$

$-(12)$

Ya we have r c by capital R equal to 1 minus X B power 1 by 3 ya this equation I will call it as 12 ya so now this is 13 so substituting equation 13 in this and then integrating directly you will get in terms of time and then conversions, okay. So when you do that what you get is substituting equation 13 in 12, okay I will write here using equations 12 and 13 what you get is t equal to this mathematics you have to do R B b k g not C Ag 1 minus 1 minus X B to the power of n plus 1 by 3 by n plus 1 plus 1 minus 1 minus X B k s by k g not so this is the equation this is equation number 14 that is the equation I think we will stop here you have to go no ya we will stop here and then try to discuss this in the tomorrow tomorrow we will try to discuss about this (())(32:51) equation and k g not you know k g not is based on r initially time t equal to 0, right ya. So again ofcourse you can also simplify this saying that okay when film alone controlling or reaction alone controlling that we will discuss tomorrow.