Chemical Reaction Engineering II
Prof. Ganesh Vishwanathan
Department of Chemical Engineering
Indian Institute of Technology, Bombay

Lecture - 28
Fluid-solid non-catalytic reactions II

Friends, let us summarize what we have learnt in the last lecture. So, in the last lecture we initiated discussion on the fluid solid non catalytic heterogeneous reactions. We looked at what are the different modes based on the nature of the nature of the non catalytic heterogeneous reaction. That is, if the size of the particle which is actually involved in the reactions size of the solid which is involved in the reaction. If that changes, if the size changes or if the particle actually, the size of the particle remains constant throughout the reaction.

So, based on that the the mode of heterogeneous reaction can be different and the resistances that are actually involved are different. And we also described initiated 2 different types of models: One is the progressive model progressive conversion model the other 1 is the shrinking core model. And then we looked because most of the reactions follow the shrinking core model. We initiated the writing balances to capture the size of the particle as a function of time for this shrinking core model. So, let us … And also we discussed on different processes which may be rate controlling and then let us continue from there.

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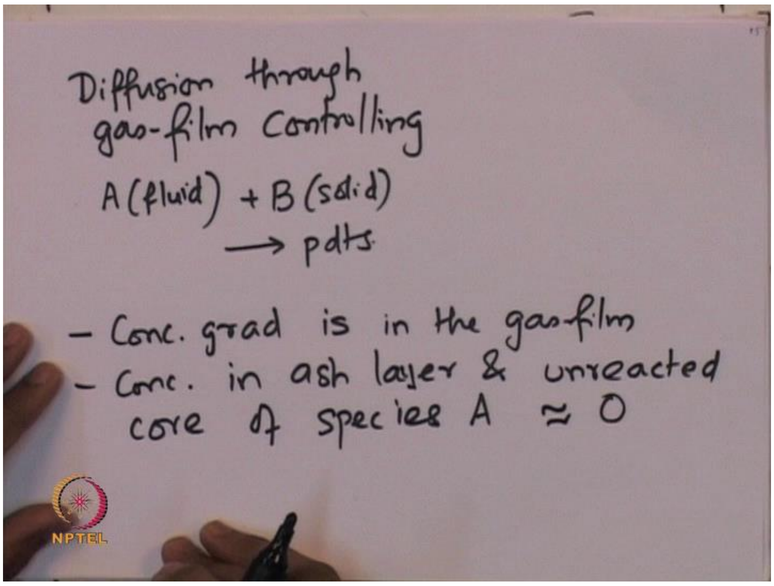

Diffusion through
gas-film Controlling

$A(\text{fluid}) + B(\text{solid}) \longrightarrow \text{pdts.}$

- Conc. grad is in the gas film
- Conc. in ash layer & unreacted core of species A ≈ 0

So, suppose if diffusion through the gas film controls the overall conversion then if the reaction is let us say A species a which is in the fluid stream, reacts with solid B which is in the in the particle core and that leads to formation of certain products, And if we assume that the if the diffusion through the gas film is controlling which means that the concentration gradient is essentially is in the gas film.

Then as all the other process is that is diffusion through the ash layer which is basically consists of the inert material and the product that may actually stick to the stick firmly to that layer and the unreacted core which is present inside the ash layer. So, the diffusion through that ash layer is faster than the diffusion of the reactant species through the gas film. And also if the reaction that occurs at the interface of the ash layer and the unreacted core; if that is also very fast. Then it means that the concentration in ash layer and in unreacted core of species A is approximately 0.

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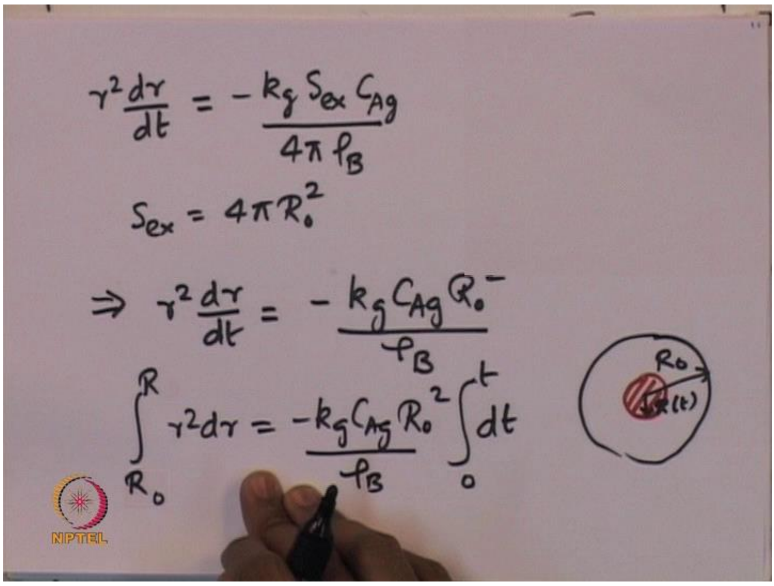

$$r^2 \frac{dr}{dt} = -\frac{k_g S_{ex} C_{Ag}}{4\pi \rho_B}$$

$$S_{ex} = 4\pi R_0^2$$

$$\Rightarrow r^2 \frac{dr}{dt} = -\frac{k_g C_{Ag} R_0^{-}}{\rho_B}$$

$$\int_{R_0}^{R} r^2 dr = -\frac{k_g C_{Ag} R_0^2}{\rho_B} \int_0^t dt$$

.

So, which means that the in the time scales where the diffusion of the species occurs these the concentration in the ash layer and the unreacted core of the species is approximately 0. Now, so we wrote a model in the last lecture and the model is that captures the change rate of change of the radius of the particle. Because of the heterogeneous reaction heterogeneous fluid solid reaction is given by r square dr by dt minus equal to minus kg which is the mass transport coefficient into the external surface area multiplied by the concentration of the species in the gas phase divided by 4 pi into the density of the catalyst; density of the solid which is participating in the heterogeneous reactions not catalyst.

So, now the external we are we have assumed that it is a spherical particle. So, therefore, S external is equal to 4 pi into R naught square where R naught is the initial radius of the particle. And the size does not change except that the unreacted core starts shrinking due to the occurrence of the heterogeneous reaction. So, substituting this expression we find that r square dr by dt that is equal to minus kg CAg into R naught square divided by rho B. So, that is the model equation and if and now if we integrate this expression, then we will be able to find out what is the how the radius changes with respect to time.

So, now we can integrate this expression between R naught and R remember that R is the … Suppose, if this is the particle and the unreacted core is actually present somewhere in the centre and the R naught is the initial radius of this particle and R is the radius of the unreacted core which is a function of time. So, we can integrate this expression between R naught and R which will tell us what is the speed at which or what is the radius as a function of time. So, r square dr that is equal to time d t.

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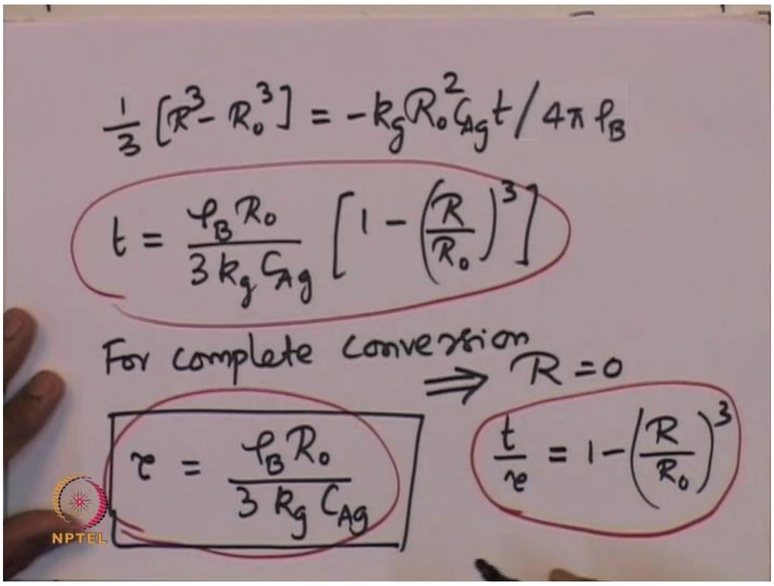

$$\frac{1}{3}\left[R^3 - R_0^3\right] = -k_g R_0^2 C_{Ag} t / 4\pi \rho_B$$

$$t = \frac{\rho_B R_0}{3 k_g C_{Ag}} \left[1 - \left(\frac{R}{R_0}\right)^3\right]$$

For complete conversion $\Rightarrow R = 0$

$$\boxed{\tau = \frac{\rho_B R_0}{3 k_g C_{Ag}}}$$

$$\frac{t}{\tau} = 1 - \left(\frac{R}{R_0}\right)^3$$

So, now integrating this expression we can find that the relationship between the instantaneous radius of the unreacted core as a function of other properties and time is given by 1 by 3 R cube minus R naught cube. That is equal to minus kg R naught square which is the square of the radius of the initial particle initial core, which contains the solids which is available for the reaction to occur and that multiplied by CAg into time. So, that is the expression for the radius as a function of time.

Now, so we we can rearrange this expression and you can find that time taken for reaching a certain core radius is given by divided by R by R naught the whole cube. Now, from this expression we can find out what is the time that is required for complete conversion. Now, complete conversion is achieved when all of the solid core has actually being consumed for reaction to form the necessary products. So, for complete conversion complete conversion R is equal to 0 that is the radius of the unreacted core has to be 0, which means that, all of the solid which is available as reactant is now consumed. So, suppose tau is the time taken for complete conversion. So, for this expression setting R equal to 0 we can find out that tau is equal to rho b R naught divided by 3 into kg into CAg. So, that is the time required for complete conversion of the solid which is present in the unreacted in the core for to form the products. So, now, by using the expression for complete conversion, we can now write the find out the ratio of the time taken to reach a particular radius divided by the time taken for the complete conversion.

So, that is given by 1 minus R by R naught cube and that is essentially obtained by taking a ratio of this expression and this expression. So, if we take a ratio of these 2 expressions we will find what is the what is the time what is the fraction or a time taken in order to reach a particular radius R.

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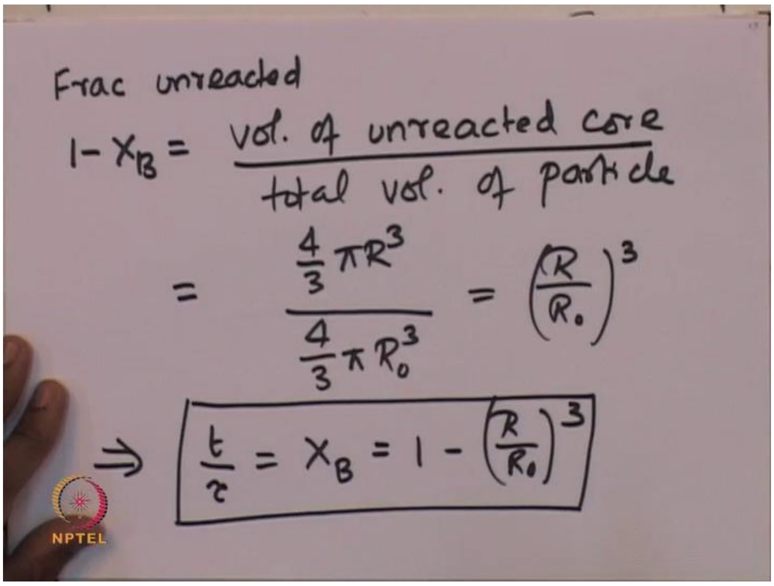

Frac unreacted

$$1-X_B = \frac{\text{vol. of unreacted core}}{\text{total vol. of particle}}$$

$$= \frac{\frac{4}{3}\pi R^3}{\frac{4}{3}\pi R_0^3} = \left(\frac{R}{R_0}\right)^3$$

$$\Rightarrow \boxed{\frac{t}{\tau} = X_B = 1-\left(\frac{R}{R_0}\right)^3}$$

So, now if we define that the fraction of fraction unreacted what is the fraction of the core which is unreacted? Then that is given by 1 minus XB, if XB is the conversion of the solid b represents the species percent in the solid. And that is equal to the volume of unreacted core divided by the total volume of the particle total. So, that is given by 4 by 3 pi R cube where is the instantaneous radius of the unreacted core divided by 4 by 3into pi R naught cube. Where R naught is the radius of the initial particle.

So, that is given by R divided by R naught the whole cube. So, therefore, from this relationship between the conversion and the instantaneous radius of the unreacted core, we can rewrite the fractional time taken to reach a particular radius as t by tau is equal to the actual conversion and that is equal to 1 minus R by R naught the whole cube. So, the fractional time taken to reach a certain radius is directly equal to the conversion if the overall conversion is actually controlled by the diffusion through the gas film.

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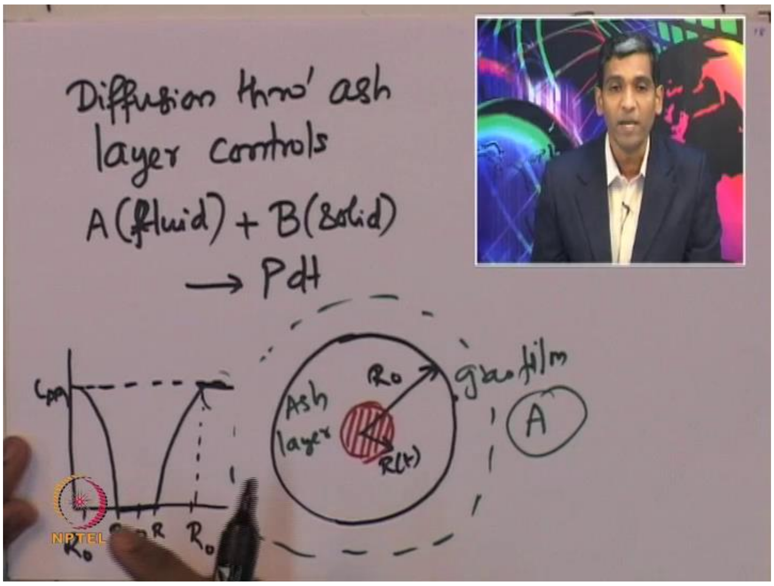

Diffusion thro' ash layer controls

A(fluid) + B(solid) $\rightarrow$ Pdt

So, next if we look at the diffusion through the ash layer, suppose if we look at diffusion through ash layer. Suppose, if we assume that the diffusion through the ash layer that is the layer which is present which means the unreacted core and the gas film. So, the species from bulk it comes to the surface of the core through the gas film and then it diffuses through the ash layer in order for it to reach the unreacted core, for the where the reaction occurs. So, suppose if the diffusion through the ash layer is actually the rate controlling step that is it is this lowest step and the other 2 that is the reaction step and the diffusion through the gas film.

If these 2 are actually very fast steps compared to the diffusion through the ash layer. Then we can now model this system assuming that the diffusion through the ash layer is the one which controls the actual process. So, in this case suppose if we assume that the reaction is species A in fluid form plus species B in solid form leads to the formation of products. It must be noted here that this stoichiometric coefficient of b can take values other than 1. And we can now suppose, if R naught is the initial … Suppose, R naught is the initial radius of the spherical particle which is actually participating in the heterogeneous reaction.

Then suppose, if there is an unreacted core and the instantaneous radius of this unreacted core let us say if this is given by R of t. So, that is the function of time and there is a gas film which is actually present around this particle. So, the gas film is present around this particle. So, this species A diffuses from gas film from the bulk to the gas film to the surface of the particle and then diffuses through the ash layers. So, this is the ash layer and diffuses through the ash layer. So, therefore, we expect that if diffusion through the ash layer is the controlling stem.

Then the concentration gradient of the species A is essentially going to be only in the ash layer in all other layers the concentration is going to be uniform. So, therefore, we can quickly sketch what is going to be the, we can intuit what is going to be the concentration profile. So, suppose if this is R naught that is the radius of particle and this is the centre of the of the sphere and this is R naught. And if this is R, that is the instantaneous radius of the unreacted core. Then we will we can expect that the if suppose this is the concentration of species in the gas phase that is the bulk concentration.

Then we can expect that the concentration profile will essentially look like this where in the bulk gas phase and in the gas film the concentration essentially reminds as the concentration as that of the bulk concentration, which is CAg or CA naught and there will be a gradient of this species a in the in the ash layer. And as soon as the species reaches the surface of the unreacted core the reaction is very fast, and therefore the reaction will immediately occur. So, the concentration of species in the unreacted core is going to be 0.

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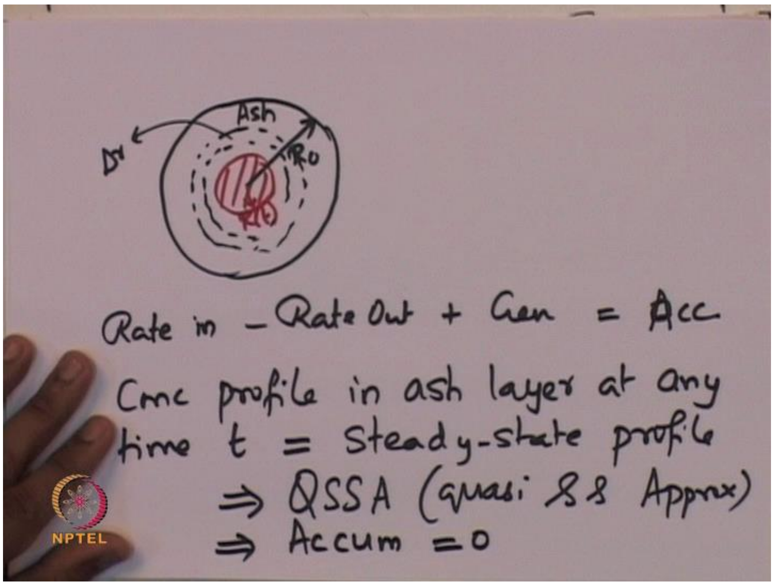

Rate in − Rate Out + Gen = Acc

Cmc profile in ash layer at any time t = Steady-state profile

$\Rightarrow$ QSSA (quasi SS Approx)

$\Rightarrow$ Accum = 0

Now, we can write a simple mole balance in order to capture the rate of change of the concentration of this species as a function of time as a function of other properties of the of this system. And this will help in estimating how the radius changes with radius of the unreacted core changes with time. So, let us write a simple mole balance. Suppose if this is the initial particle; suppose if this is the particle at any time t. And the radius of the particle is R naught remember that the it is the size of this particle is not changing.

Then if the unreacted core is present here, so that is the unreacted core whose radius is now R t that is a function of time. And suppose, if we take a small element suppose and the thickness of this element is delta R. And if we assume that the positive R is the radius of the radius going outward from the centre is the positive direction. Then we can write a mole balance where we can say that the rate at which the species is entering this element minus the rate at which the species leaves. Plus whatever is being generated that should be equal to 0 that should be equal to accumulation.

So, now if we assume that the concentration profile in the ash layer; so, this is the ash layer here. So, if we assume that the concentration profile in ash layer at any time is equal to the steady state profile which means that, if we assume a pseudo steady state or quasi steady state approximation. Quasi steady state approximation for the quasi steady, state approximation for the concentration of species in the ash layer. Then the accumulation is equal to 0. So, if we assume quasi steady state this means that the there is there is no accumulation. So, accumulation is equal to 0.

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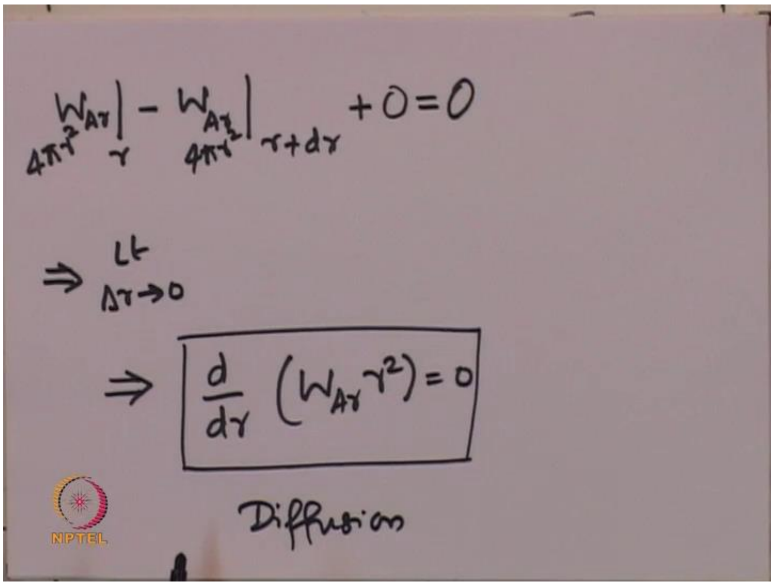

$$W_{Ar}4\pi r^2\Big|_{r} - W_{Ar}4\pi r^2\Big|_{r+dr} + 0 = 0$$

$$\Rightarrow \underset{\Delta r \to 0}{Lt}$$

$$\Rightarrow \boxed{\frac{d}{dr}\left(W_{Ar}r^2\right) = 0}$$

Diffusion

So, therefore, we can now write a mole balance where the rate at which the species enters if r is the molar flux at which the species is entering that element delta r thickness at r. So, that WAr at r is the molar flux with which the species is entering that element multiplied by 4 pi r square it is a molar flux, but the balance is written in molar rate. So, WAr which is the molar flux multiplied by the corresponding area at r.

So, WAr into 4 pi r square at r plus dr that is the rate molar rate at which the species enters this element and this is the molar rate at which the species leaves. Plus nothing is being generated because the reaction is actually occurring at the unreacted core surface. So, therefore, generation is 0 and we have assumed that it is a a quasi steady state approximation. So, therefore, the rate of change therefore, the accumulation term is also equal to 0.

So, now we can set a limit delta r goes to 0. So, then we will get the model equation will reduce to d by dr WAr in r square equal to 0. So, that is the that is the mole balance that is the that is the mole balance. Now, we need to know what is this War? WAr is the molar rate and the process with which the species is actually entering that element is the diffusion. So, the molar molar flux can actually be related to the concentration using the fixed law and. So, suppose if we assume that it is equimolar counter diffusion.

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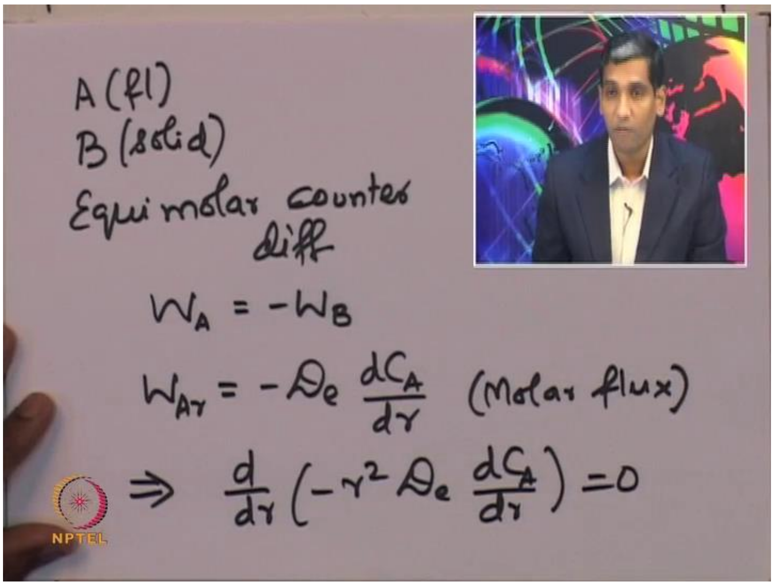

A (fl)
B (solid)
Equimolar counter diff

$$W_A = -W_B$$

$$W_{Ar} = -\mathcal{D}_e \frac{dC_A}{dr} \quad \text{(Molar flux)}$$

$$\Rightarrow \frac{d}{dr}\left(-r^2 \mathcal{D}_e \frac{dC_A}{dr}\right) = 0$$

So, because there are 2 species which is participating in the in the reaction: species A which is in the fluid phase and species B which is the solid phase. So, suppose if we assume that if it is a equimolar counter diffusion if, from stoichiometry we can actually discern. That the flux with which the species A is actually entering should be equal to the flux with which the species b is actually reacting to form a certain product.

So, therefore, WAr is given by minus De which is the effective diffusivity of the species multiplied by d CA by dr. So, plugging this into plugging the molar flux… So, this is the molar flux assuming that its equimolar counter diffusion that is the molar flux and De is the corresponding diffusivity. And plugging this into the mole balance we find that the mole balance is d by d r minus r square equal to 0. So, now we need to solve this equation in order to find concentration as a function of position.

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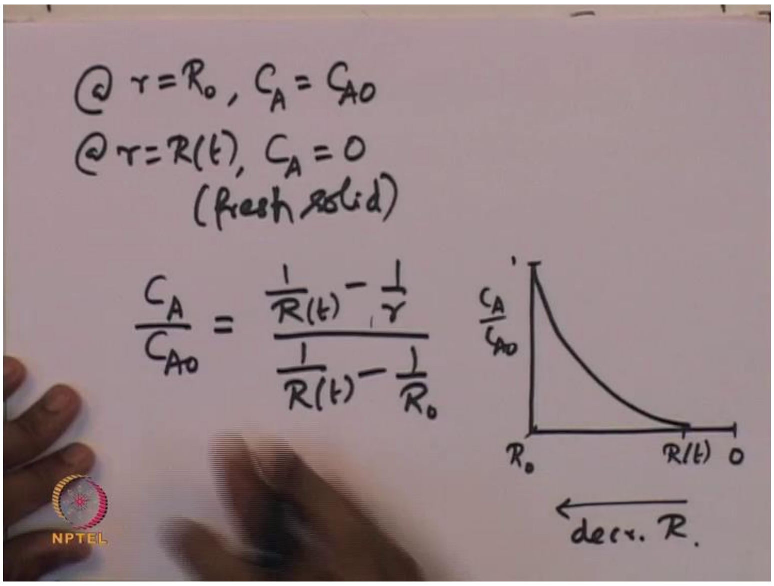

$@\ r = R_0,\ C_A = C_{A0}$

$@\ r = R(t),\ C_A = 0$

(fresh solid)

$$\frac{C_A}{C_{A0}} = \frac{\frac{1}{R(t)} - \frac{1}{r}}{\frac{1}{R(t)} - \frac{1}{R_0}}$$

So, remember that we said we will assume quasi steady state for the concentration profile in the ash layer. That is the instantaneous concentration can be assumed to be that of the of the steady state profile in the ash layer. So, the corresponding boundary conditions are at r equal to R naught which is the outer rim of the particle. And remember that the particle size does not change. So, at r equal to R naught we expect that the concentration of the species is equal to that of the bulk concentration or the gas phase bulk concentration. And at r equal to R of t which is now remember that the radius is now changing with time because the unreacted core is now shrinking.

So, CA equal to 0 because this is a diffusion ash layer diffusion controlled process and because and also at r equal to t there is a there are fresh solid is present. T he unreacted core the reactant actually experiences unreacted core which is now ready for reaction. So, on integrating we can find that the concentration is given by CA by CA naught. That is equal to 1 by r which is which is a function of time minus 1 by r divided by 1 by r minus 1 by r naught.

So, 1 by r is any position between r naught and r and R of t is the location of the unreacted core and r naught is the outer rim of the particle. So, now if I sketch the … If we sketch the concentration profile. So, if this is the centre of the sphere and this is R naught. So, that is the thickness of the sphere. So, this is decreasing Rand let us say this is R of t the unreacted core is actually present between 0 and R of t and. So, if we plot

CA by c a naught then the concentration profile essentially it looks like this. So, if decreases from 1, all the way to 0 at R of t because, the reaction actually occurs since quickly at this location.

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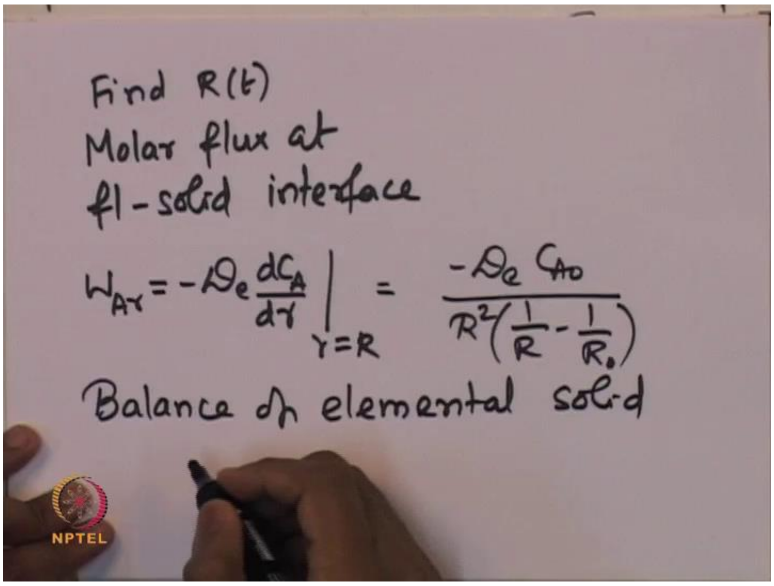

Find R(t)

Molar flux at

fl-solid interface

$$W_{Ar} = -\mathcal{D}_e \frac{dC_A}{dr}\Big|_{r=R} = \frac{-\mathcal{D}_e C_{A0}}{R^2\left(\frac{1}{R}-\frac{1}{R_0}\right)}$$

Balance of elemental solid

Now, in order to obtain the in order to obtain in order to find out what is the radius of the unreacted core, we need to find out what is the expression for R of t as a function of other properties of the system. So, now we can from because its diffusion control the molar flux at fluid solid interface, where the reaction actually occurs because it is we have assumed that its diffusion controlled in the ash layer.

So, as soon as the fluid species reaches the surface of the unreacted core the reaction is going to occur immediately. So, therefore, the molar flux at the fluid solid interface should be equal to the rate at which the reaction actually occurs. So, let us look at the molar flux at the fluid solid interface. So, molar flux will be WAr which is equal to the diffusivity D multiplied by dCA by dr at r equal to R. And that is given by minus De CA naught divided by r square into 1 by R minus 1 by R naught.

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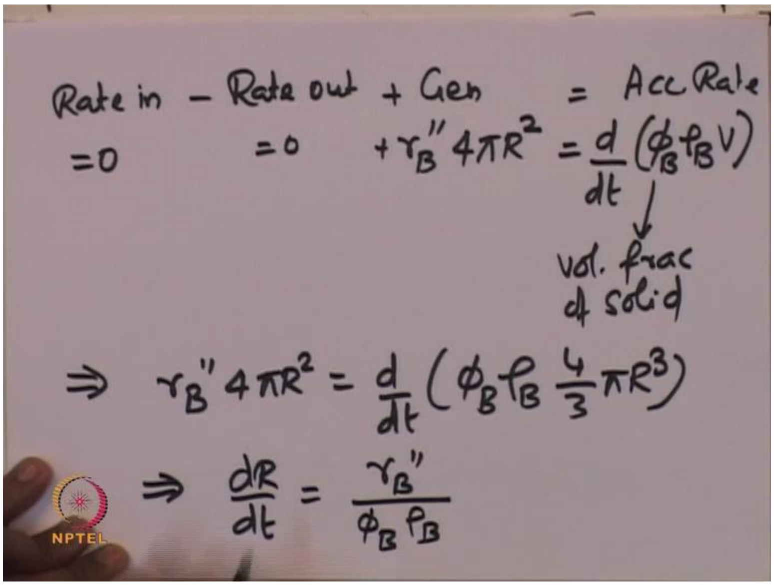

Rate in − Rate out + Gen = Acc Rate

$$=0 \qquad =0 \qquad +r_B'' 4\pi R^2 = \frac{d}{dt}(\phi_B \rho_B V)$$

vol. frac of solid

$$\Rightarrow r_B'' 4\pi R^2 = \frac{d}{dt}\left(\phi_B \rho_B \frac{4}{3}\pi R^3\right)$$

$$\Rightarrow \frac{dR}{dt} = \frac{r_B''}{\phi_B \rho_B}$$

Now, because the reaction occurs immediately the rate at which the molar flux molar flux at which the species actually reaches the unreacted core, should be equal to the multiplied by the area should be equal to the amount of reaction that occurs. So, therefore, we can now write a balance on the elemental solid. We can write a balance on elemental solid in order to relate the rate of reaction and the flux. So, the rate at which the solid that actually enters in the ash layer which is equal to 0 minus the rate at which the solid leaves the ash layer that is equal to 0.

The rate at which it is being generated is basically the rB is the reaction rate multiplied by the area of the unreacted core because, the reaction actually is occurring on the surface of the unreacted core. And the solids are not moving therefore, the rate in and the rate out are 0 and this is the generation term and that should be equal to the accumulation rate. And the accumulation rate is essentially given by d by dt of phi B rho B into the volume of the particle now phi B is nothing, but the volume fraction of the unreacted core which is occupied by the solid.

So, now plugging in the expression for the volume of the unreacted core we can rewrite the balance as rB 4 pi R square that is equal to d by dt pi r cube. On simplifying this expression, we will find that dr by dt which is the rate at which the unreacted core radius changes with time and that is equal to divided by phi B into rho B. So, now because the it is a its diffusion controlled in the ash layer; soon after this species reaches the surface of the solid unreacted core the reaction is going to occur immediately.

So, therefore, the rate of reaction should be equal to the molar flux the flux of reaction should be equal to the flux at which the reactant is actually reaching the surface the surface of the unreacted core.

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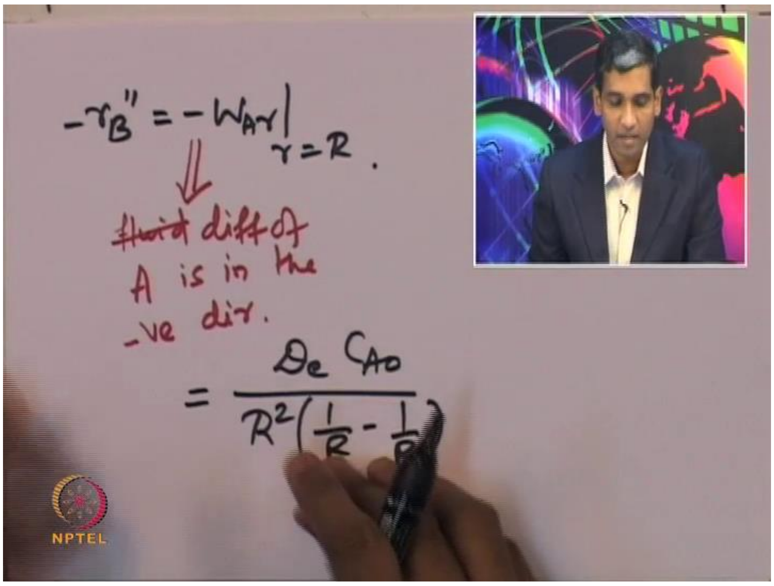

$$-r_B'' = -W_{Ar}\Big|_{r=R}.$$

$\Downarrow$

~~fluid~~ diff of A is in the -ve dir.

$$= \frac{\mathcal{D}_e C_{A0}}{R^2\left(\frac{1}{R} - \frac{1}{R}\right)}$$

So, therefore, rB that should be equal to minus WAr at r equal to r. So, remember that the minus sign here is essentially refers to the fact that the fluid because the diffusion of species the fluid diffusion of species A is in the negative direction.

So, we said that the sign convention is we assume that the outwards direction is positive and the diffusion of this species a is actually going from outside to the inside of the particles. So, therefore, the diffusion is actually in the negative r direction and that is why there is a minus sign that has been inserted here. And that should be equal to Definitions CA naught divided by R square into 1 by R minus 1 by R naught. So, this expression relates the rate at which the solid is being consumed for reaction and the other properties of that system.

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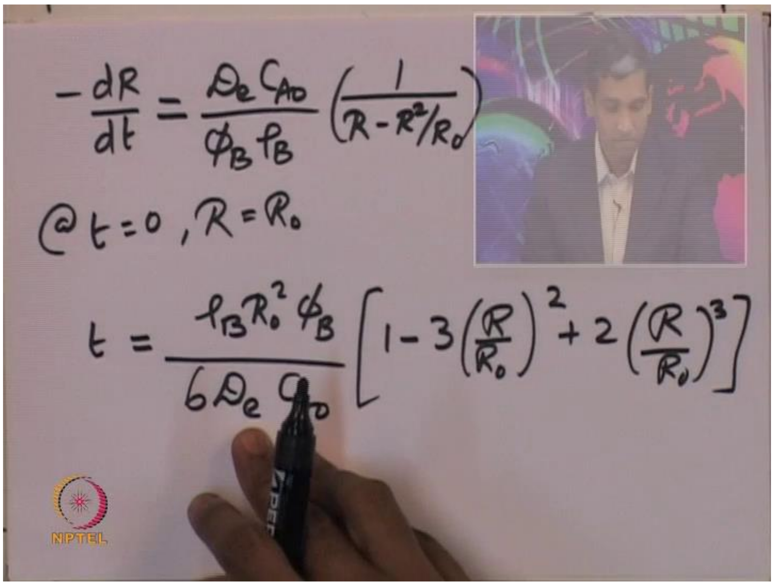

$$-\frac{dR}{dt} = \frac{D_e C_{A0}}{\phi_B \rho_B}\left(\frac{1}{R - R^2/R_0}\right)$$

$@\ t = 0,\ R = R_0$

$$t = \frac{\rho_B R_0^2 \phi_B}{6 D_e C_{A0}}\left[1 - 3\left(\frac{R}{R_0}\right)^2 + 2\left(\frac{R}{R_0}\right)^3\right]$$

So, from here we can find out the we can rewrite the expression for the for dr by dt which is the rate at which the radius changes with time that is equal to divided by 1 by R minus R square by R naught. So, now we can integrate this expression at time t equal to 0 that is when the reaction has not started. Then the size of the unreacted core is equal to r naught.

So, we can integrate this expression ad we can find that the time taken to reach a certain radius of the unreacted core is given by rho B R naught square into phi B, which is the volume fraction of the unreacted core. Which is occupied by the solid divided by 6 into diffusivity into CA naught multiplied by 1 minus 3 R by R naught square plus 2 into R by R naught cube.

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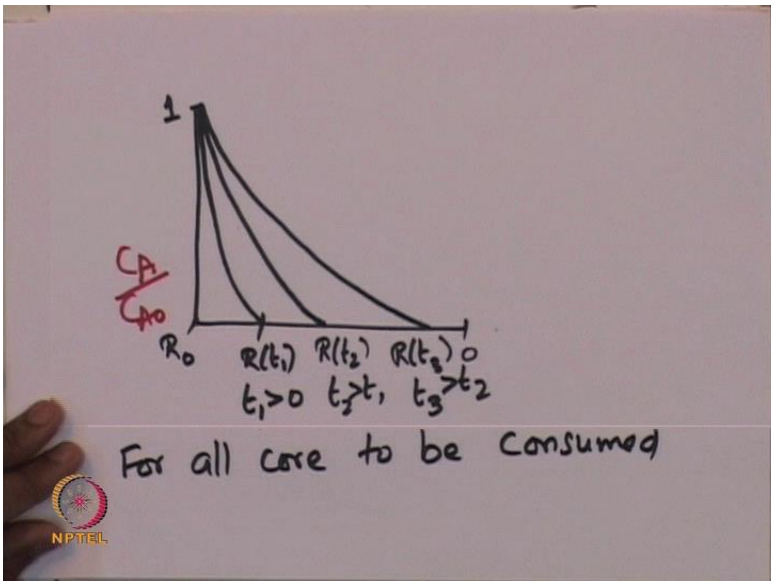

For all core to be consumed

So, that is the expression for that is the relationship between the time that is taken to reach a certain radius and the other properties of this system. So, now, if attempt to understand the radius the radius of the unreacted core as a function of time that can actually be captured in this graph. So, suppose if this is the centre of the particle and this is the outer rim of the particle that is the initial radius of the unreacted core. So, suppose if we look at c the amount of species which is actually being consumed.

So, if we plot CA by CA naught. So, that actually reduced with position. So, if R t 1 is the radius of the unreacted core let us say at time t 1. And if you assume that t1 is greater than 0 and at a later time further reaction would have occurred and the unreacted core would have shrunk a little more. So, this will be R of t2 this will be the profile with at time t2 where, t2 is now greater than t1. And then at a much later time the profile would be … So, that is the concentration of species as a function of position at various times.

So, as we can see that as the reaction proceeds the ash layer increases and therefore, the species A has to penetrate. So, therefore, species a therefore, species a actually penetrates into the ash layer and as a function of time the there will be more ash which is formed around the unreacted core. And therefore, we can see this is the concentration profile. So, now, for all of the core to be consumed. So, for all to core to be consumed which means that, the unreacted solid actually goes to complete conversion.

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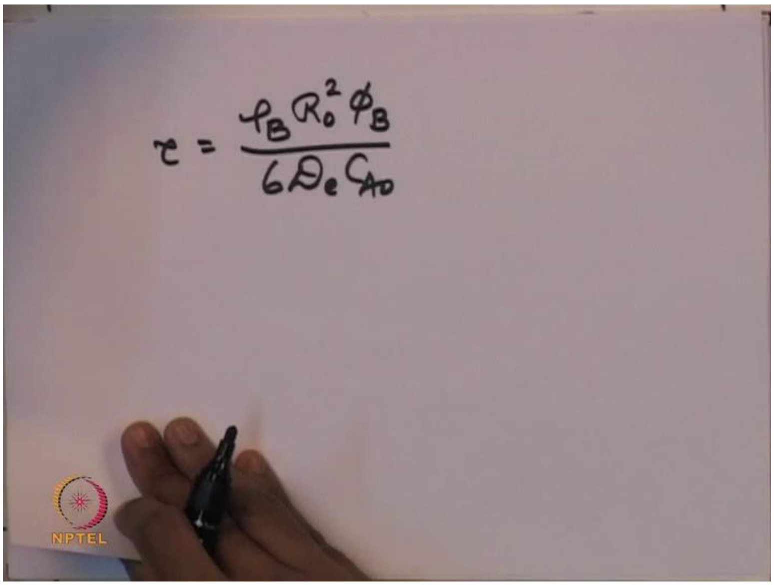

$$\tau = \frac{\rho_B R_0^2 \phi_B}{6 D_e C_{A0}}$$

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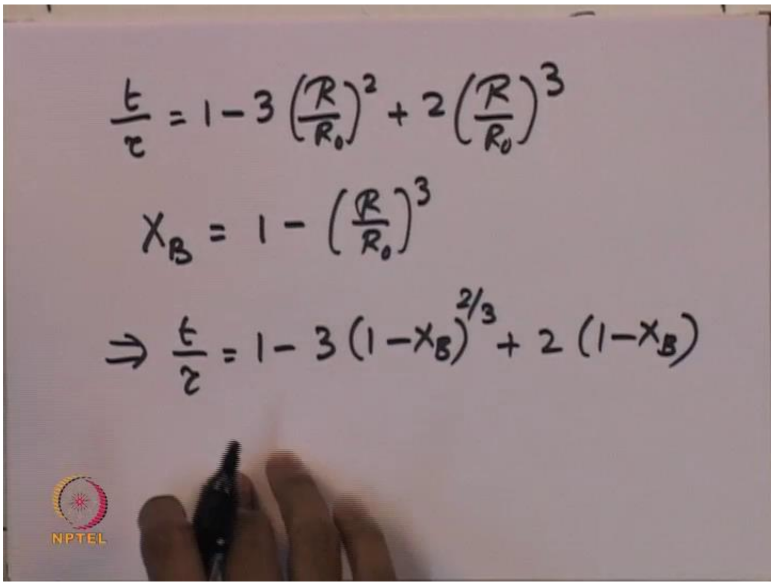

$$\frac{t}{\tau} = 1 - 3\left(\frac{R}{R_0}\right)^2 + 2\left(\frac{R}{R_0}\right)^3$$

$$X_B = 1 - \left(\frac{R}{R_0}\right)^3$$

$$\Rightarrow \frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$$

That the time that it takes for complete conversion can be estimated as tau which is equal to rho B which is the density of the particle multiplied by R naught into phi B divided by 6 De into CA naught. So, that is the time taken for complete conversion that is all of the solid which is present in the original particle has now been consumed because of the reaction.

So, using this expression we can find out that t by tau which is the ratio of time taken to reach certain radius, because of this reaction divided by the time taken for complete conversion. That is given by 1 minus 3 into R by R naught square plus 2 into R by R naught cube. So, suppose if we define conversion xB as before as 1 by R by R naught the whole cube.

Then t by tau can be written as 1 minus 3 into 1 minus xB which is the conversion of the solid which is present in the in the particle plus 2 into 1 minus xB. So, this is the relationship between the time taken for the core to reach a certain location and the corresponding conversion. And the conversion is; obviously, a function of the size of the unreacted core. So, now, the third process which may control the overall reaction is the actual reaction that is occurring in the surface of the unreacted core.

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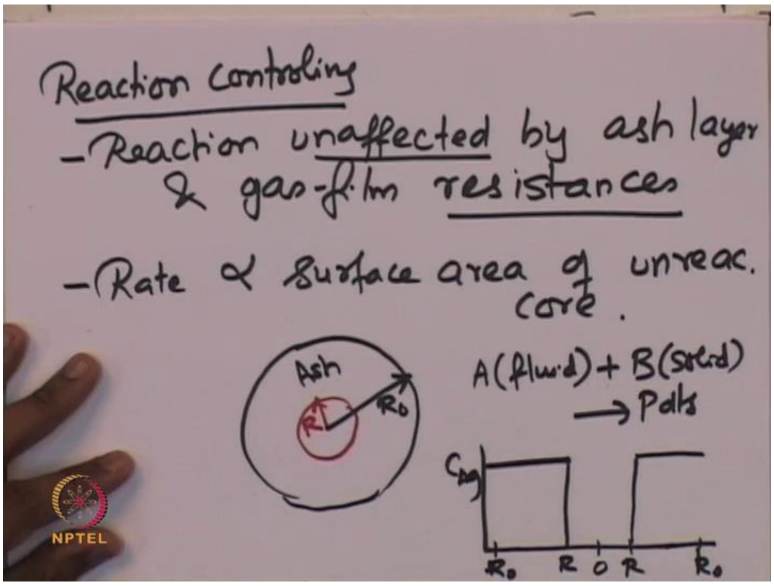

Reaction controlling

- Reaction unaffected by ash layer & gas-film resistances

- Rate $\propto$ surface area of unreac. core.

A(fluid) + B(solid) → Pdts

So, suppose if we assume that its reaction controlling, now what it means is that the reaction the reactant species now it defuses through the gas film and it defuses through the ash layer and then it reaches the surface of the unreacted core. Now, if the reaction is the reaction that is occurring on the surface of the unreacted core with the solid its controlling the overall reaction. Then it means that that is the slowest step and the diffusion that is occurring though the gas phase gas film and also through the ash layer is actually phi is actually fast.

So, which means that the reaction is unaffected by ash layer and film resistances, so this is unaffected by the ash layer and the gas film resistances. And also it suggests that the rate should be proportional to the surface area of the unreacted core. So, rate must be proportional to the surface area of the unreacted core. So, suppose if we depict the particle. So, here is a particle and the initial radius of the particle is R naught and the ash layer and the unreacted core at anytime t lets say if that as R and the ash layer which is actually present around is between R and R naught.

Then if A in the fluid form and B in the solid form reacts to give products, then one could intuit what is going to be the concentration profile. So, because the reaction is the one which is controlling the concentration of the species in the gas phase in the gas film and also in the ash layer will be the concentration of the species in the bulk gas stream itself.

Because, it is a very fast process and the reaction with the slow process; so we expect; that the concentration of the species between R and R naught. So if this is R naught, will be equal to the concentration of the species in the gas phase. This is the centre of the core and as soon as it reaches the surface it will undergo reaction. So, there is no concentration in gradient inside the core.

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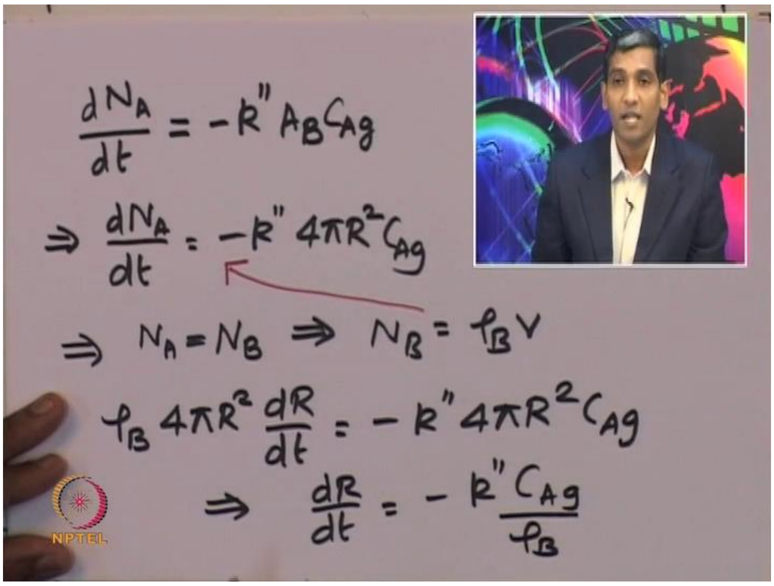

$$\frac{dN_A}{dt} = -k'' A_B C_{Ag}$$

$$\Rightarrow \frac{dN_A}{dt} = -k'' 4\pi R^2 C_{Ag}$$

$$\Rightarrow N_A = N_B \Rightarrow N_B = \rho_B V$$

$$\rho_B 4\pi R^2 \frac{dR}{dt} = -k'' 4\pi R^2 C_{Ag}$$

$$\Rightarrow \frac{dR}{dt} = -\frac{k'' C_{Ag}}{\rho_B}$$

So, now we can write a mole balance in order to capture the change in the change in the radius of the core as a function of time. So, suppose if NA is the number of moles of a, which is actually reacting than dNA by dt which is the rate at which the number of moles of A is being moles of a is being consumed because of reaction.

So, that should be equal to minus k prime into the area of the unreacted core multiplied by the corresponding gas phase concentration. So, that is basically the rate at which the reaction is actually occurring. So, now substituting the area of the surface; instantaneous area of the unreacted core. That is given by dNA by dt is given by minus k prime into 4 pi R square, where R is the radius of the unreacted core at any point in time multiplied by CAg . So, now NA the number of moles of the species gas reactant should be equal to the number of moles of the solid which is actually reactant by based on stoichiometry.

So, expressing that … So, NA equal to NB and an NB equal to rho B into the volume of the unreacted core. So, now plugging in this expression plugging in this relationship into the mole balance we find that we can rewrite the mole balance as rho B into our pi R square into dr by dt. That is equal to minus k double prime into CAg. So, we can simplify this mole balance as dr by dt that is equal to minus k prime, which is the intrinsic specific rate constant in CAg divided by the density of the of unreacted core.

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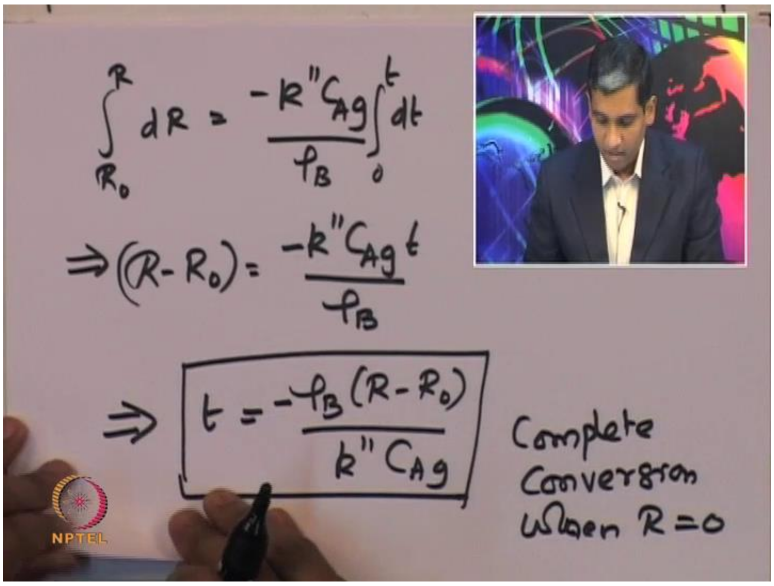

$$\int_{R_0}^{R} dR = \frac{-k''C_{Ag}}{\rho_B}\int_{0}^{t} dt$$

$$\Rightarrow (R-R_0) = \frac{-k''C_{Ag}\,t}{\rho_B}$$

$$\Rightarrow \boxed{t = \frac{-\rho_B(R-R_0)}{k''C_{Ag}}}$$

Complete Conversion when $R=0$

So, now we can integrate this expression to find out the find out the radius of the unreacted core as a function of time and other properties. So, that is given by R naught is the initial particle size and suppose at any instant in time R is the size of the unreacted core that is equal to k prime CAg divided by rho B integral between 0 to t dt. So, from here we can find that R minus R naught divided by rho B. So, we can rearrange this expression to find that the time at which a certain radius can be reached is given by rho B into R minus R naught divided by k double prime to CAg.

Now, what is the time taken for reaching complete conversion? The complete conversion can be achieved, when R is equal to 0. So, there should be a minus sign here. So, where the complete conversion can be achieved when R is 0; when r equal to 0, that is all of the core all of the solids which is present in the core has actually completely reacted. So, now, with that we can find out what is the time required for complete conversion.

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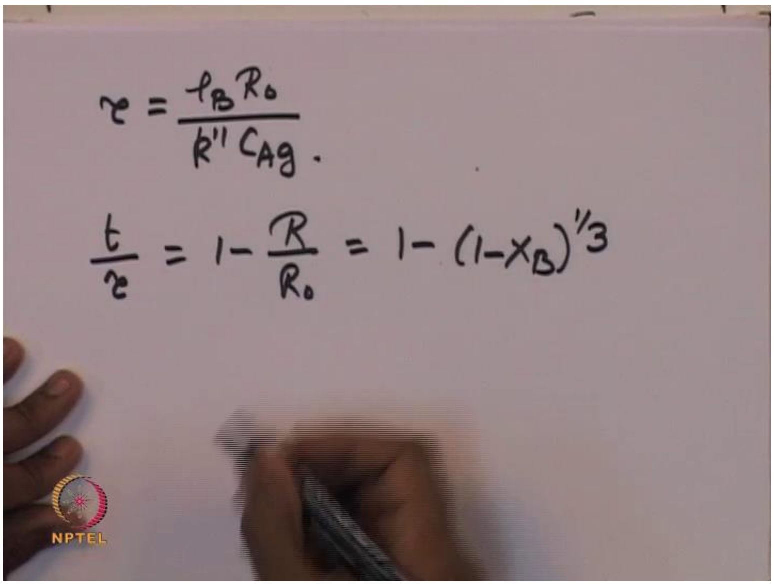

$$\tau = \frac{\rho_B R_0}{k'' C_{Ag}}.$$

$$\frac{t}{\tau} = 1 - \frac{R}{R_0} = 1 - (1 - x_B)^{1/3}$$

So, if tau is the time required for complete conversion that is given by rho B into R naught divided by k double prime into CAg. So, using this expression we can write we can find out what is the fractional time required for reaching the a particular radius at this t by tau that is given by 1 minus R by R naught. And that is equal to 1 minus 1 minus xB to the power of 1 by 3. So, that is the relationship between the fractional time taken to reach a particular radius and the corresponding conversion if the system is reaction controlling.

So, now we looked at 3 particular cases where we looked at what is the relationship between the fractional time taken with respect to conversion for if the system is diffusion controlling through the gas film. If the if it is diffusion controlling through the ash layer or if it is reaction controlling all of these for a case where the particle size does not change. That is the as when the reaction occurs an ash layer is formed where the ash layer may contain inert solids or the product which may firmly bind to the layer where the solids have already reacted.

Now, the next question is we looked at 2 moles earlier 2 modes of these kind of fluid solid non catalytic reactions, where 1 case where the size of the particle remain same; the other case where the size actually start shrinking. So, in the case of where the size start shrinking, we can now look at what are the different rate controlling steps and what are ways to find out what is the radius of the unreacted core as a function of time.

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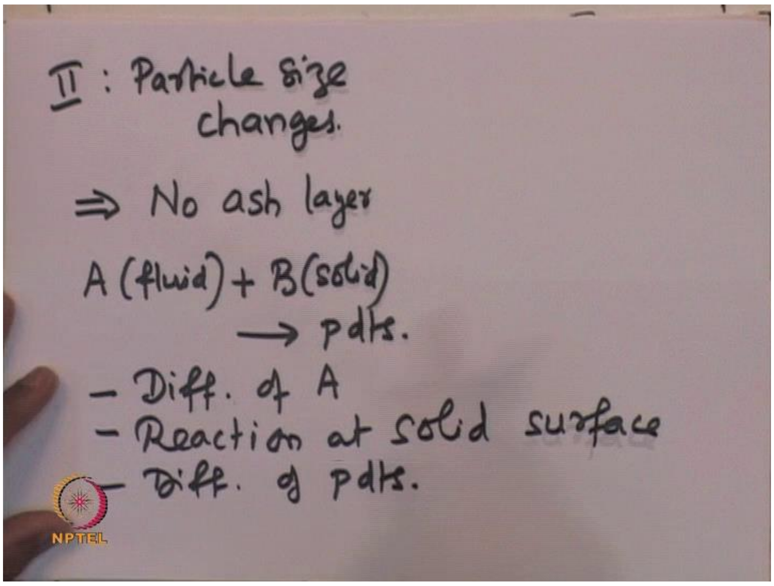

II : Particle size changes.

⇒ No ash layer

A (fluid) + B (solid) ⟶ pdts.

- Diff. of A
- Reaction at solid surface
- Diff. of pdts.

So, now second mole is where the particle size changes. Now, particle size changes it immediately implies that there is no ash layer. We assume here theta the density variation due to reaction is negligible that is, the density of solid product and reactants are not very difficult, if the densities are different the particle size can change even if ash layer is present. The number of steps that may control the overall conversion actually decreases for what we have seen in the first case where the particle sign does not change. Because, there is no ash layer that is present and therefore, the diffusion through the ash layer can be ignored now.

That is the resistance for diffusion though ash layer does not exist for this particular case. So, suppose as before we assume that A species A which is in the fluid phase stream reacts with species B, which is in the solid phase to form certain products. Now, the different steps that are actually involved in this case is basically diffusion of species A that is, mass transfer of from bulk to unreacted core or gas film diffusion. And then reaction at the solid surface and then diffusion of the products back into the gas stream. So, it is the gas stream.

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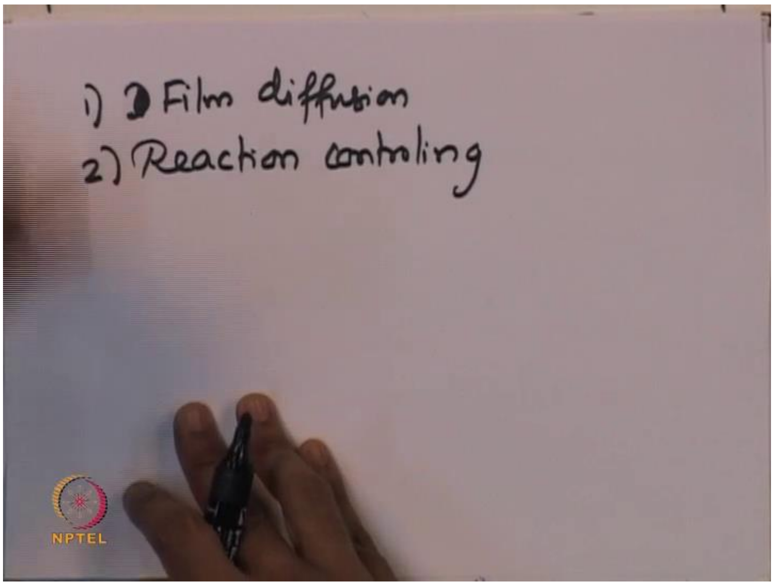

1) Film diffusion
2) Reaction controling

So, there is ash layer. So, therefore, there is no diffusion through the ash layer. So, what are all the different processes that may actually control the overall conversion: the first one would be film diffusion controlling. So, the gas film which is actually present around the core which is actually undergoing this fluid solid non catalytic reaction. So, that diffusion through that film might actually control the overall reaction or it might be reaction controlling.

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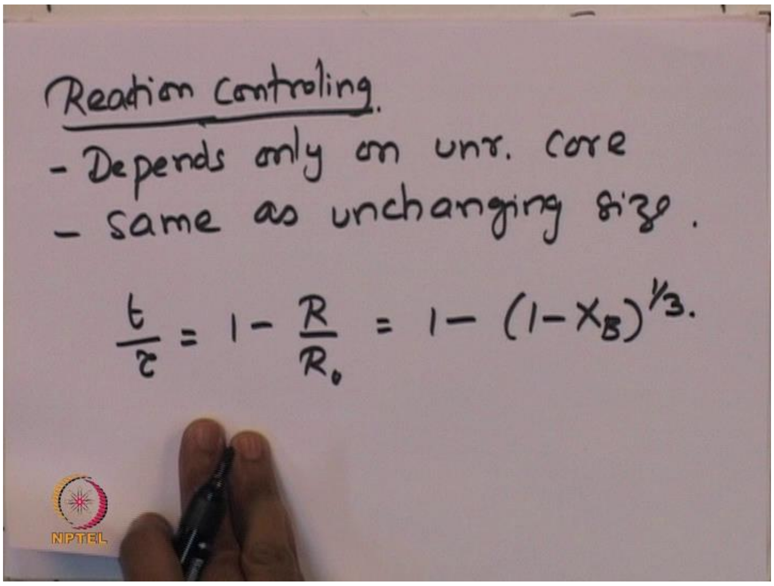

Reaction controling.

- Depends only on unr. core
- same as unchanging size.

$$\frac{t}{\tau} = 1 - \frac{R}{R_0} = 1 - (1 - X_B)^{1/3}.$$

So, let us start looking at the reaction controlling process. So, suppose if the overall reaction is overall conversion is controlled by reaction; its reaction controlling. Suppose, if its reaction controlling then, because if it is reaction controlling it means that the reaction with a slower step and all the other processes are correspondingly faster. So, therefore, the presence of the gas film around is actually irrelevant to the actual process that is occurring because it is a fast process. And therefore, it depends it is going to depend only on the unreacted core which is which is present and which is participating in the reaction.

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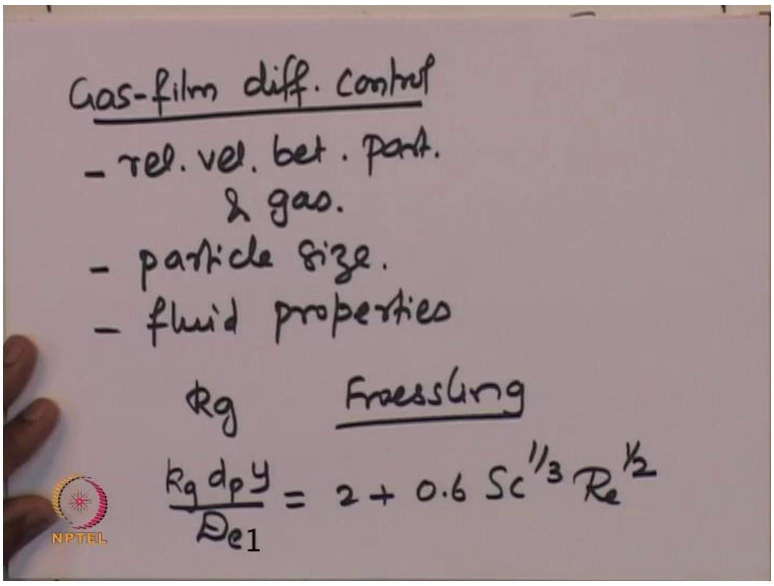

Gas-film diff. control

- rel. vel. bet. part. & gas.
- particle size.
- fluid properties

k_g Froessling

$$\frac{k_g d_p y}{D_{e1}} = 2 + 0.6\, Sc^{1/3} Re^{1/2}$$

So, it depends only on the unreacted core and it is same as what same as the reaction controlling same as the system of system where the reaction is controlling the overall conversion in the case of the particles where the size of the particle was not changed. And that is the previous mode that we had looked at. So, its same as unchanging size. So, therefore, we can easily read that the fraction of time taken to reach a certain radius you simply given by 1 minus R by R.

So, plugging this into plugging the molar flux. So, this is the molar flux assuming that its equimolar counter diffusion that is the molar flux and d e is the corresponding diffusivity and plugging this into the mole balance we find that the mole balance is d by d r minus r square equal to 0. So, now, we need to solve this equation in order to find concentration as a function of position.

So, remember that we said we will assume steady state for the concentration. So, remember the reaction is actually conducted in a reactor where the particles are now moving relative to that of the gas phase. So, therefore, the relative velocity plays an important role as to how much resistance that the gas phase actually offering to offering to transport o the reactants from the bulk gas phase to the surface of the unreacted core.

Another major factor is the size of the particle itself another factor on all other fluid properties they may also affect the resistance that is offered by the gas film. So, there are several correlation which are available for estimating mass transport coefficient under the gas film diffusion control. So, remember that the resistance that is offered by the diffusion of the reactants species through the gas film is essentially captured in the mass transport coefficient a g just like what we have seen for the earlier mode.

There are several correlations which are available and 1 good correlation is by it is called the Froessling correlation. And that correlation is given by kg diameter of the particle dp multiplied by the mole fraction of the species in the gas phase divided by the corresponding diffusivity. And that should be equal to 2 plus 0.6 into Schmidt number to the power of 1 by 3 and Reynolds number to the power of 1 by 2.

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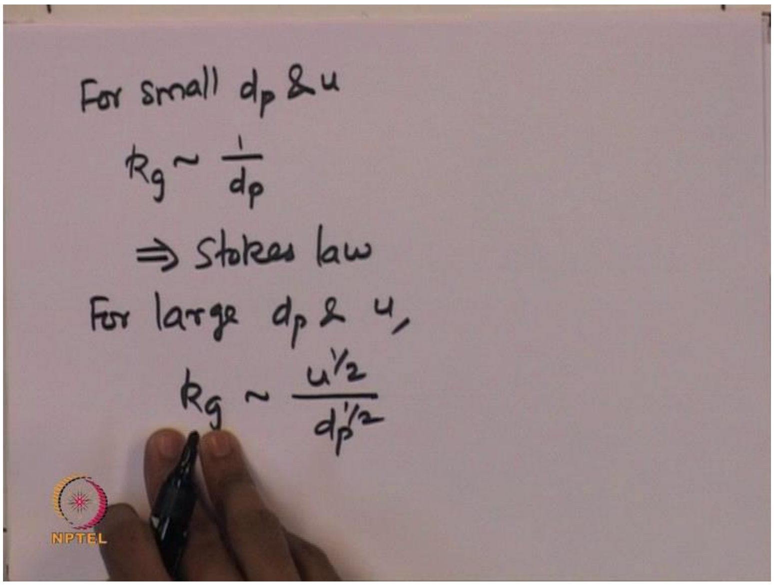

For small d_p & u

$$k_g \sim \frac{1}{d_p}$$

⇒ Stokes law

For large d_p & u,

$$k_g \sim \frac{u^{1/2}}{d_p^{1/2}}$$

So, Schmidt number is nothing but the ratio of kinematic viscosity to the corresponding diffusivity effected diffusivity of that species. And the Reynolds number is initially the dimensionless quantity that captures the corresponding fluid low properties. So, now if the if the particle size is very small. So, for small dp and small velocity u, the mass transport coefficient for if you look at the if you actually do a little, but of algebra on the on the correlation. One can actually discern that the mass transport coefficient approximately scales as one over diameter of the particle.

So, under these conditions this the Stokes law can actually be applied in order to find out the estimate the radius of the particle as a function of time when the when the unreacted core is undergoing a certain fluid solid non catalytic reaction. Now, for large dp large particle size and large velocities then the mass transport coefficient scales as u to the power of half that is the velocity square root o velocity divided by the square root of particle. So, let us take the case of stokes law stokes law regime.

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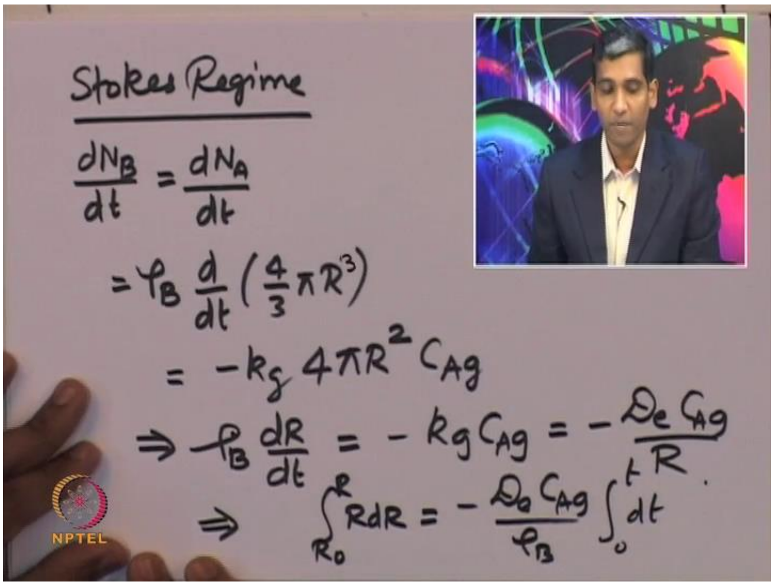

Stokes Regime

$$\frac{dN_B}{dt} = \frac{dN_A}{dt}$$

$$= \rho_B \frac{d}{dt}\left(\frac{4}{3}\pi R^3\right)$$

$$= -k_g 4\pi R^2 C_{Ag}$$

$$\Rightarrow -\rho_B \frac{dR}{dt} = -k_g C_{Ag} = -\frac{D_e C_{Ag}}{R}.$$

$$\Rightarrow \int_{R_0}^{R} R\,dR = -\frac{D_e C_{Ag}}{\rho_B}\int_0^t dt$$

So, let us take the case of stokes regime in stokes regime the mole balance dNB by dt which is the rate of change of this solid species with respect to time and that is equal to dNA by dt. And that is equal to rho B which is the density of the solids into d by dt of 4 by 3 pi R cube, where R is the radius of the unreacted core unreacted core which is actually changing in size due to the reaction. And that should be equal to minus kg which is the mass transport coefficient multiplied by the surface area of the unreacted core surface multiplied by the concentration of the reactants species in the bulk gas phase.

So, from here we can write that rho b into dr by dt that is equal to minus kg into CAg. But, in the Stokes regime the mass transport coefficient essentially is the ratio of the diffusivity divided by the radius of the particle. So, that is given by minus De into CAg divided by R. So, now integrating this expression we can find that integral R naught to R R dR that is equal to minus De CAg divided by the density into integral 0 to t d t.

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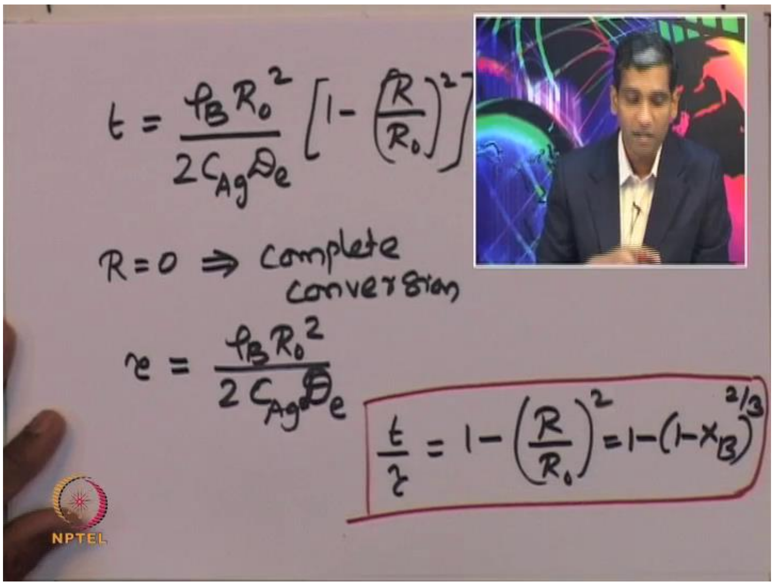

$$t = \frac{\rho_B R_0^2}{2 C_{Ag} D_e}\left[1-\left(\frac{R}{R_0}\right)^2\right]$$

$R = 0 \Rightarrow$ complete conversion

$$\tau = \frac{\rho_B R_0^2}{2 C_{Ag} D_e}$$

$$\boxed{\frac{t}{\tau} = 1-\left(\frac{R}{R_0}\right)^2 = 1-(1-x_B)^{2/3}}$$

So, this expression this model actually provides a relationship between the radius of the particle as a function of time. So, now, integrating we can find out what is the time that is taken for reaching a certain radius. So, time t is given by rho B R naught square divided by 2 times CAg into the effective diffusivity 1 minus R by R naught the whole square. So, that is the time taken by the unreacted taken by the particle to reach a certain radius R because of the heterogeneous gas solid reaction.

So, now in order to achieve complete conversion, complete conversion means all of the power all of the solids present in the particle has actually been complete consumed. Consume, which means that r equal to 0 corresponds to complete conversion. So, under these conditions we can find out that the time taken for complete conversion is given by rho B R naught square divided by 2 CAg into Definitions; which is the diffusivity of the diffusivity of the species through the particle.

So, the fractional time that is taken to reach a certain radius of the unreacted core is essentially given by 1 by 1 minus R by R naught square that is equal to 1 minus 1 minus x b to the power of 2 by 3. So, this expression can be obtained simply by taking the ratio of these 2 expressions which are present here. So, now we can easily find out from this expression that the ratio the fractional time that is taken here is actually proportional to 1 minus conversion to the power of 2 by 3.

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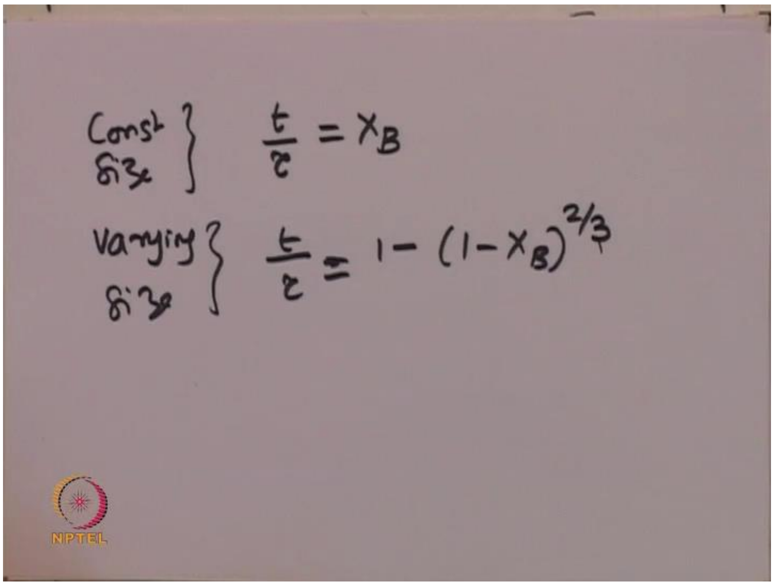

Const size $\Big\}$ $\frac{t}{\tau} = x_B$

Varying size $\Big\}$ $\frac{t}{\tau} = 1 - (1 - x_B)^{2/3}$

Now, if we compare what is the corresponding expression in the case of the particles where the size of the particle does now change, there it is a completely different expression. And that is actually given by in the case of constant size if we compare we will see that if the film diffusion is controlling. Then the case of constant size the fractional time that is taken is equal to the conversion itself. And while for the varying size t by tau is actually given by one minus 1 minus xB to the power of 2 by 3.

It is important to note that the conversion here is actually reflects the size of the unreacted core and the conversion here actually reflects the size of the unreacted core in the varying size. So, therefore, clearly there is a big difference in the time that is taken for the particle to reach a certain size. Where if the particle size is constant or the particle size is actually particle is actually shrinking because of the reaction.

So, what we have seen in today’s lecture is we have looked at how to capture the radius of the unreacted core as a function of time. And other properties of the system when there is different processes that may be controlling the overall reaction. So, this we have done for 2 different case where both the modes that is: the mode where the particle size does not change with respect when the due to the heterogeneous reaction. And for the mode where the particle size actually shrinks because of the heterogeneous reaction between the fluid and the solid.

Thank you.