Chemical Reaction Engineering - II

Prof. Ganesh A Viswanathan
Department of Chemical Engineering
Indian Institute of Technology- Bombay

Lecture – 46
Fluid-Solid Non-Catalytic Reactions IV

So, now you if I attempt to understand the radius of the unreacted core as a function of time that can actually be captured in this graph.

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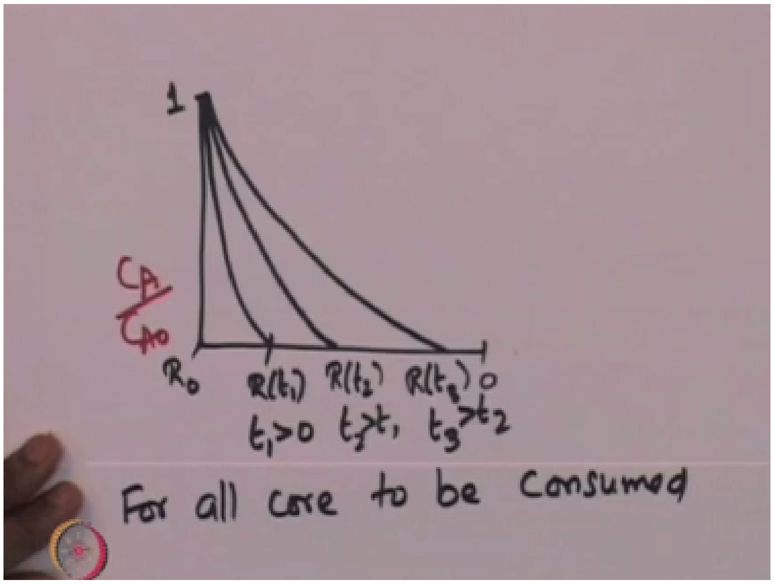

So, suppose if this is the center of the particle and this is the outer rim of the particle that is the initial radius of the unreacted core and so suppose if we look at the amount of species is actually being consumed. So, if you plot CA by CA0 so that actually reduces with position so if Rt1 is the radius off the unreacted core let us say at time t1 and if you assume that t1 > 0 and at a later time further reaction would have occurred.

And the unreacted core shrunk a little more and so this will be R of t2 this will be the profile with at the 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 A as a function of a position at various time. 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 actually penetrates into the ash layer and as a function of time we 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 core to be consumed which means that unreacted solid actually goes to complete conversion that the time that it takes for complete conversion can be estimated as tau = rho B.

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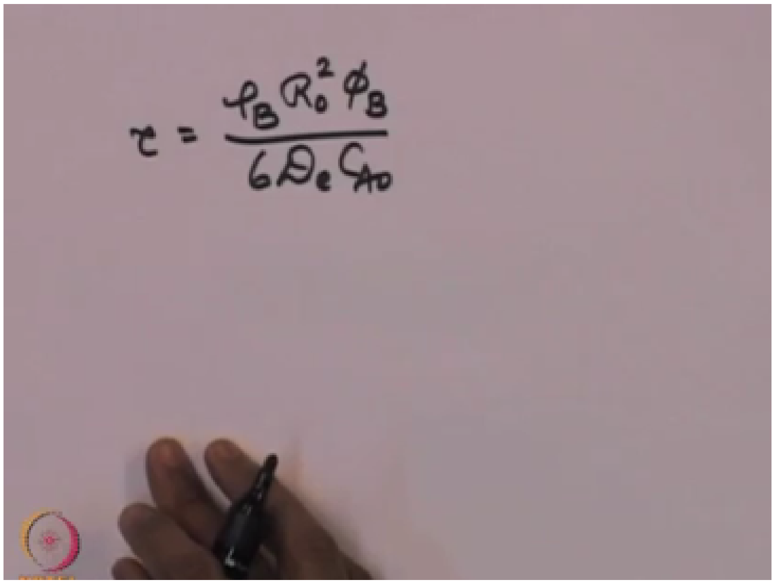

$$\tau = \frac{\rho_B R_0^2 \phi_B}{6 D_e C_{A0}}$$

Which is the density of the particle multiplied by R0* Phi B /6De*CA0 and 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/tau.

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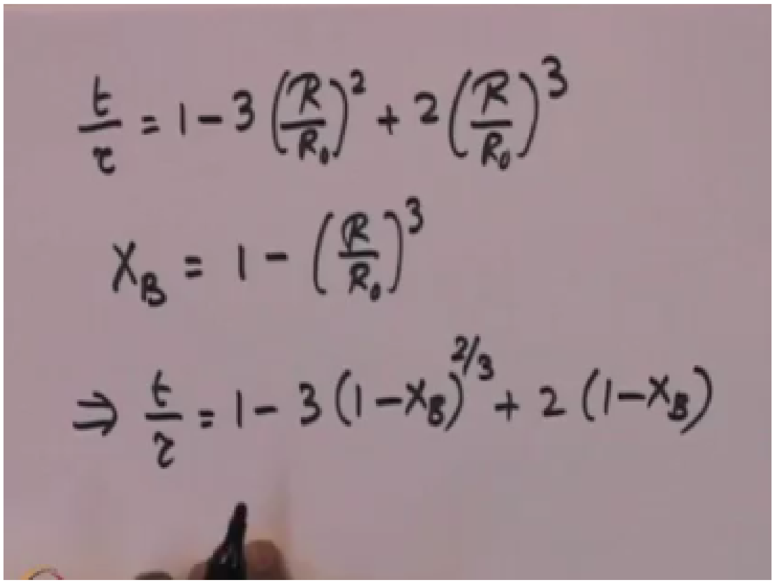

$$\frac{t}{\tau} = 1 - 3\left(\frac{R}{R_0}\right)^2 + 2\left(\frac{R}{R_0}\right)^3$$

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

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

Which is the ratio of time taken to reach a certain radius because of this reaction divided by the time for complete conversion that is given by 1 – 3*R/R0 square +2*R/R0 3 so suppose if we define conversion XB as before as 1 – R/R0 the whole 3 then t/tau can be written as 1-3*1-XB which is the conversion of the solid which is present in the particle + 2*1- 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 3rd process which may control the overall reaction is the actual reaction that is occurring in this surface of the unreacted core so suppose if we assume that it is reaction controlling.

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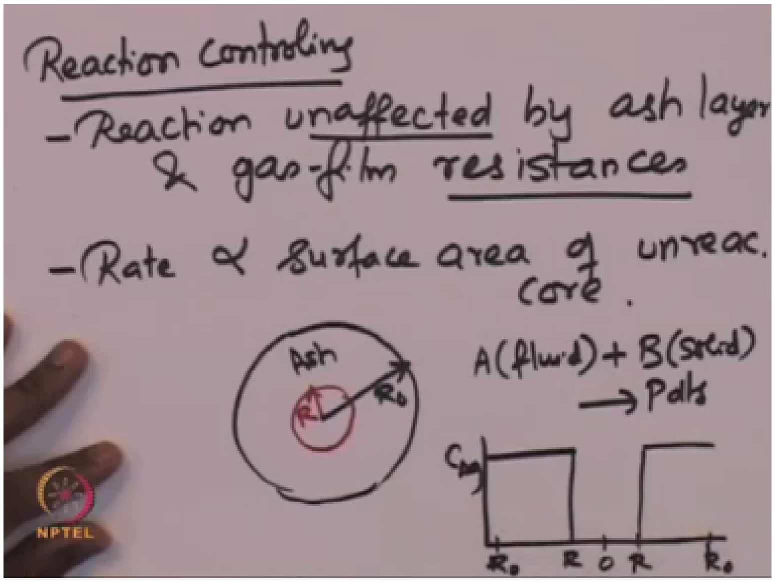

Reaction controling

- Reaction unaffected by ash layer & gas-film resistances

- Rate ∝ surface area of unreac. core.

$A(\text{fluid}) + B(\text{solid}) \rightarrow \text{Pdts}$

Now what it means is that the reaction, the reaction species now it diffuses through the gas-film and it diffuses through the ash layer and then it reaches the surface of the unreacted core or if the reaction that is occurring on the surface of the unreacted core with the solid is controlling the overall reaction then it means that is the slowest step and the diffusion that is occurring through the gas is gas film.

And also through the ash layer is actually fire is actually fast and so which means that the reaction is unaffected by ash layer and gas film resistances and 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 suppose if we depict the particle so here is the particle and the initial radius of the particle is R0and the ash layer.

And the unreacted core at any time t let us say if that as R and the ash layer which is actually present around is between R and R0 then if A in the fluid form and B in the solid form reacts to give products then 1 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 of the slow process and so we expect that the concentration of the species between R and R0 so if this is R0 will be equal to the concentration of the species in the gas phase and this is the center of the core and as soon as it reaches the surface it will undergo reaction and so there is no concentration in a gradient inside the core.

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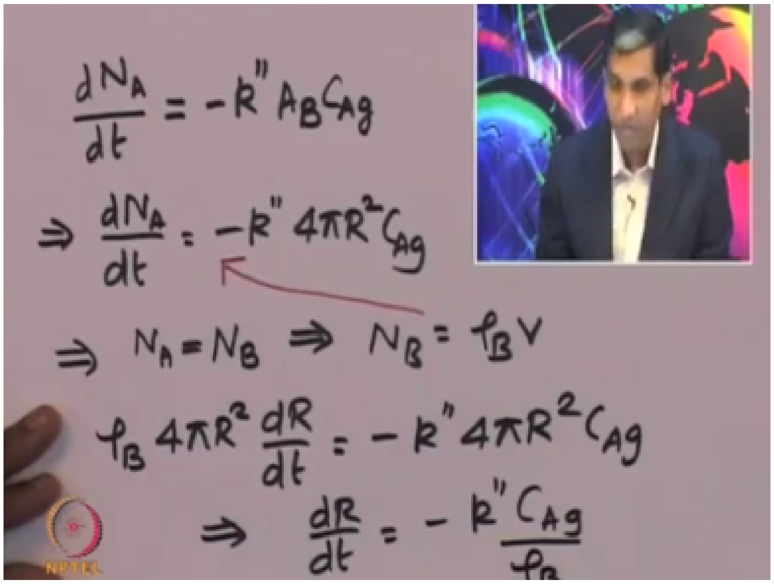

$$\frac{dN_A}{dt} = -k'' A_B C_{Ag}$$

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

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

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

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

So, now we can write a mol balance in order to capture the change in the concentration 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, then dNA/dt which is the rate at which the number of moles of A is B moles of A is being consumed because of reaction so that should be = -K 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/ dt is given by –K prime * 4 Phi R square where R is the radius of the unreacted core at any point in time multiplied by CAg so now NA number of moles of the species gas reactant should be = number of moles of the solids which is actually reactant by based on the documentary.

And so expressing that so NA = NB and an NB = Rho B * volume of the unreacted core so now plugging in this expression talking in this relationship into the mole balance we find that we can rewrite the mole balances As Rho B *4Phi R square *dR/dT that = -K double prime *CAg so we can simplify this mole balances dR/dt that = - K prime which is the intrinsic specific rate constant in CAg/the density of the unreacted core.

So, now we can integrate this expression to find out the radius of the unreacted core as a function of time and other properties.

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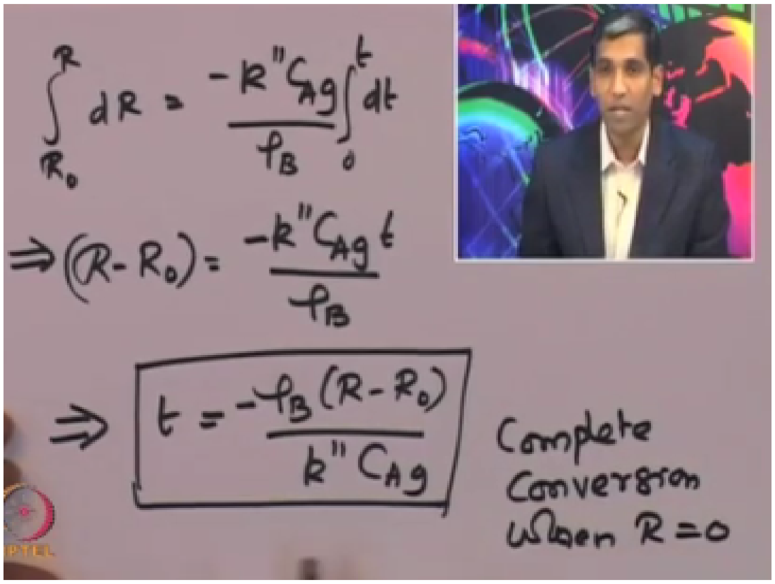

$$\int_{R_0}^{R} dR = \frac{-k'' C_{Ag}}{\rho_B}\int_{0}^{t} dt$$

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

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

Complete conversion when $R = 0$

So, that is given by R0 is the initial particle size and suppose at any instant in time R is the size of the unreacted core that = k prime CAg /Rho B integral between 0 to t dt so from here we can find that R – R0 / by Rho B and so we can rearrange this expression to find that the time which at which certain radius can be reached is given by Rho B * R-R 0/ K double prime * CAg now what is the time taken for reaching complete conversion.

The complete conversion can be achieved when R = 0 so there should be a - sign here so where the complete conversion can be achieved when R is 0 when all of the core and all of the solids which is present in the core has actually completely reacted.

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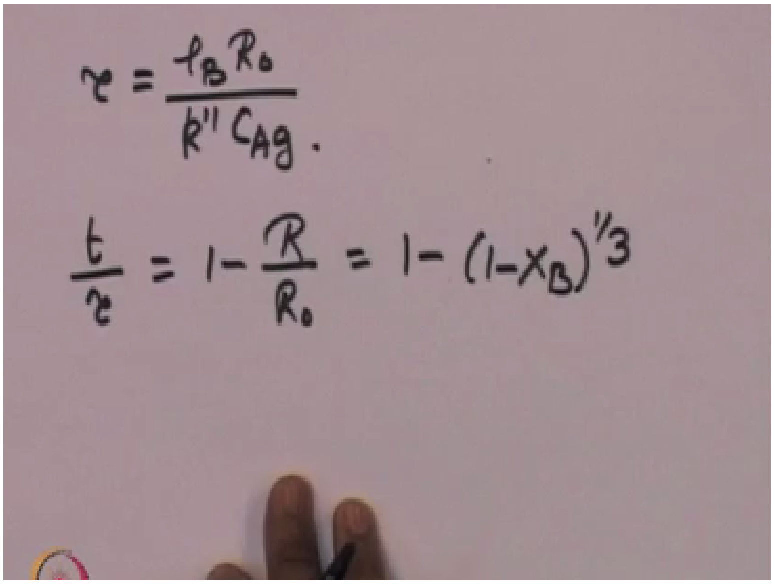

$$\tau = \frac{\rho_B R_0}{k'' C_{Ag}} .$$

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

So, now with that we can find out what is the time required for complete conversion so if tau is the time required for complete conversion that is given by Rho B * R0/ k double prime* CAg. Using this expression, we can drive we can find out what is the fractional time required for reaching a particular radius that is t/tau that is given by 1 – R by R0 and that = 1- 1-XB to the power of 1/3.

So that is the relationship between the fractional time taken to reach a particular radius and the corresponding conversion if the system is reaction control 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 the diffusion controlling through the gas film 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, and ash layer is formed where the ash layer may contain inert solids or the products which may firmly bind to the layer where the solids have already reacted. Now the next question is we looked at 2 modes earlier 2 modes of this kind of fluid solid non-catalytic reactions where 1 case where the size of the particle remains same.

The other case where the size actually starts shrinking so in the case of where the size starts shrinking, we can now look at what are the different rate controlling steps and what are the ways to find out what is the radius of the unreacted core as a function of time.

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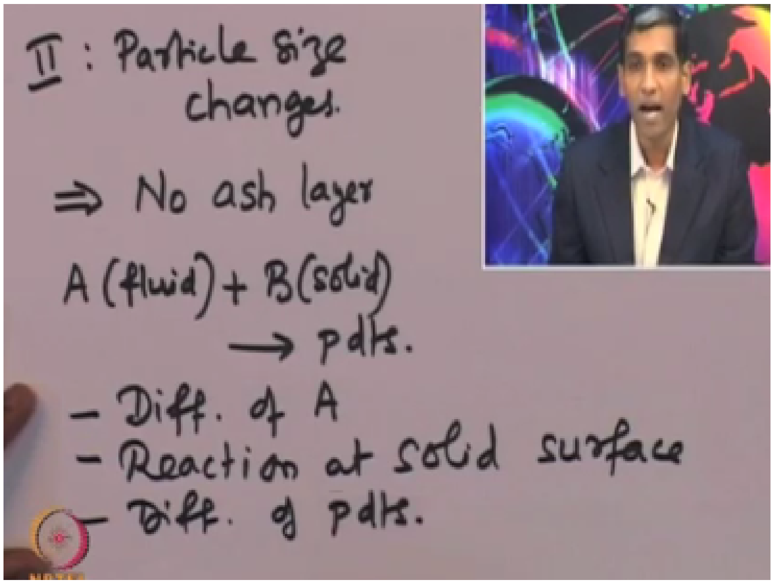

II : Particle size changes.

$\Rightarrow$ No ash layer

A (fluid) + B (solid) $\rightarrow$ pdts.

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

So, now 2nd mode is where particle size changes now if particle size changes it immediately implies that there is no ash layer, we assume here that the density variation due to reaction is negligible that is the density of solid product and reactants are not very different 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 from 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 through the 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 A 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 there is no 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.

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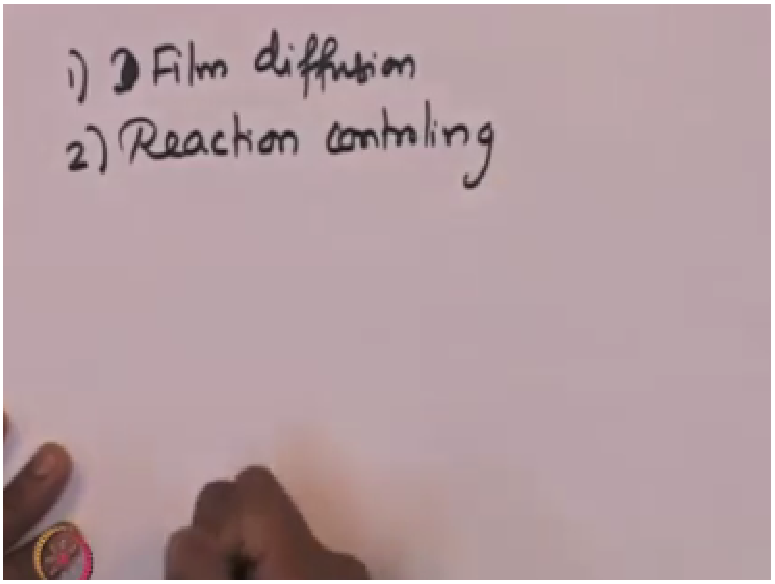

1) Film diffusion
2) Reaction controlling

The 1st would be film diffusion controlling so the gas film which is actually present around the core which is actually undergoing as this fluid solid non catalytic reaction so that diffusion through that film might actually control the overall reactions or it might be the reaction controlling so let us start looking at the reaction controlling process.

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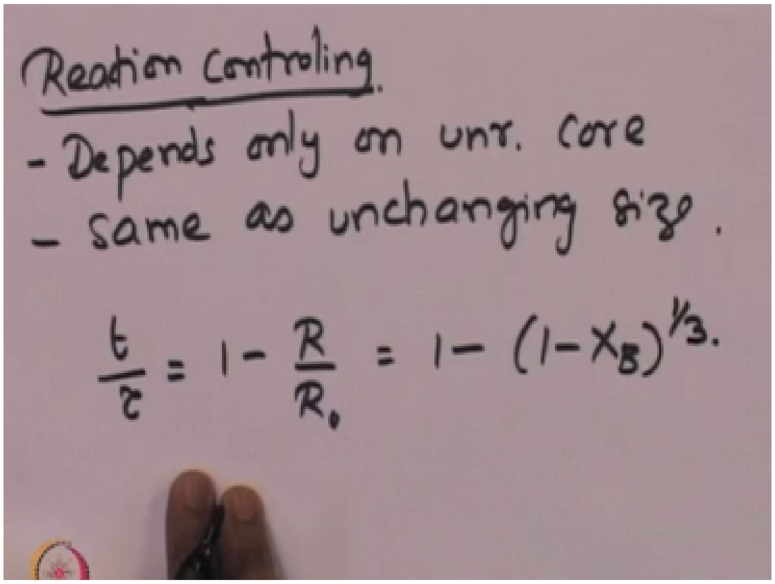

Reaction controling.

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

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

So, suppose if the overall reaction is overall conversion is controlled by the reaction so reaction controlling suppose if it is reaction controlling then because the if it is a reaction controlling it means that the reaction the slowest 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 the it depends going to depend only on the unreacted core which is which is present, and which is participating in the reaction, so it depends only on the unreacted core and it is same as the reaction controlling really 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 changing.

That is the previous mode that we had looked at, so it is same as unchanging size so therefore we can easily read that the fraction of time taken to reach a per a certain radius is simply given by 1 – R/ R0 and that is given by 1 – 1- XB to the power of 1/3 now suppose if you let look at the next case as if the overall conversion is actually controlled by the gas phase diffusion.

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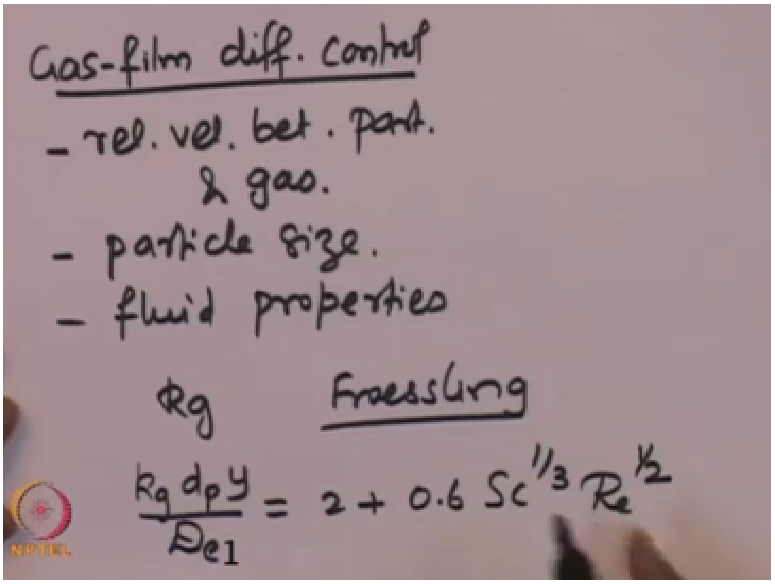

Gas-film diff. control

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

kg   Froessling

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

So, if it is a gas - film diffusion control suppose if the overall reaction is controlled by the diffusion through the gas film then the film resistance is the resistance offered for transport of species from the bulk to the surface of the unreacted core is actually controlled by many different factors and some of the factors are the what is the relative velocity between particle and the gas stream or the fluid stream.

So, remember that 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 film is actually offering to transfer offering to transport of the reactants from the bulk gas phase to the surface of the unreacted core the 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 correlations 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 reactant species through the gas film is essentially captured in the mass transport coefficient kg just like what we have seen for the earlier more.

And there are several correlations which are available, and 1 correlation is by it is called the Froessling correlation and that correlation is given by kg diameter of the particle DP * by the mole fraction of the species in the gas phase divided by the corresponding diffusivity and that should be = 2+0.6* Schmidt number to the power of 1/3 and Reynolds to the power of ½.

So Schmidt number is nothing but the ratio of kinematic viscosity to the corresponding diffusivity effective of that species and the Reynolds number is essentially the dimensionless quantity that captures the corresponding fluid flow properties.

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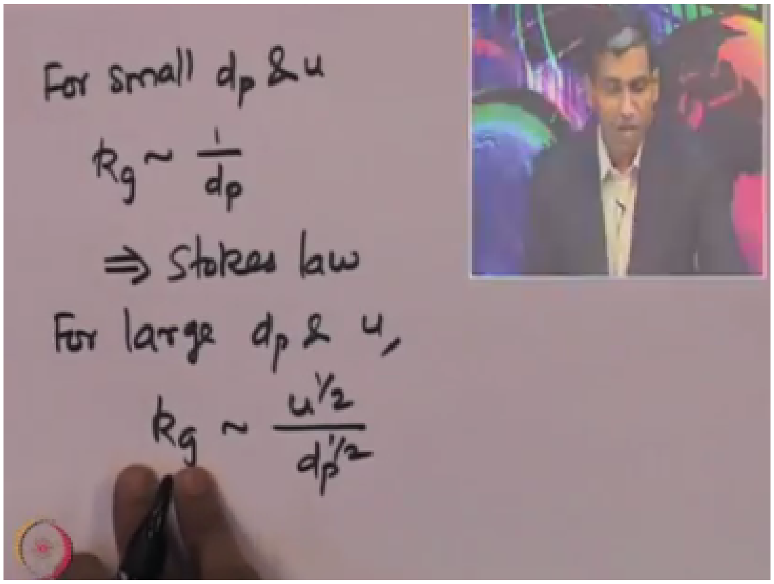

For small d_p & u

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

$\Rightarrow$ Stokes law

For large d_p & u,

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

So, now if the particle size is very small so for small DP and small velocity u the mass transport coefficient from if you look at if you actually do a little bit of algebra on the correlation one can actually discern that the mass transport coefficient approximately scales as 1 over diameter of the particle so under these conditions 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 unreacted core is undergoing a certain fluid solid non catalytic action now for large dp large particle size and large velocities then the mass transport coefficient scales as u to the power of 1/2 that the velocity square root of velocity / square root of particle so let us take the case of stokes law regime and let us take the Stokes regime.

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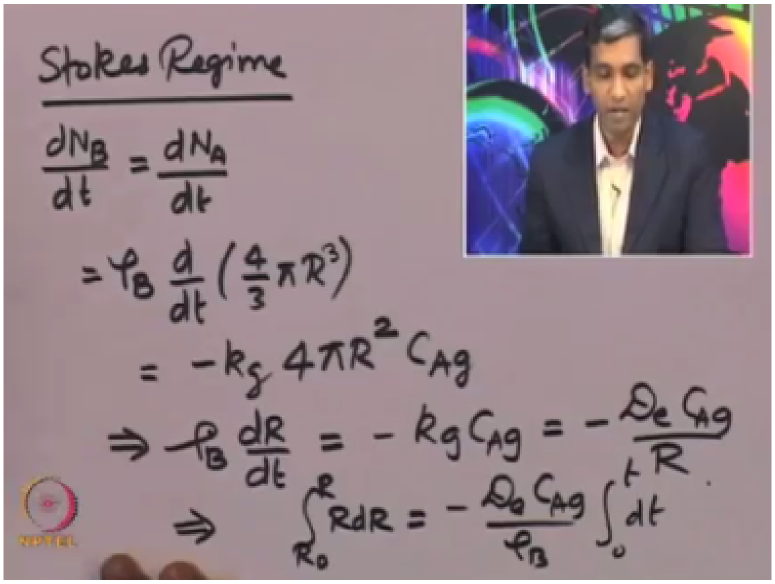

Stokes Regime

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

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

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

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

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

In stokes regime the mole balance dNB/dt which is the rate of change of the solid species with respect to time and that = dNA/dt and that =Rho B which is the density of the solids * d/dt of 4/3 Pi R cube where R is the radius of the unreacted core which is actually changing in size due to the reaction and that should be = - kg which is the mass transport coefficient multiplied by the surface area of the unreacted core surface * by the concentration of the reactant species in the bulk gas phase.

So from here we can write that Rho B* dR/dt that = -kg * CAg but in the stokes regime the mass transport coefficient essentially is the ratio of the diffusivity divided by the radius of the particle and so that is given by – De * CAg/R so now integrating this expression we can find that integral R0 to R RdR that = - DeCAg/ density* integral 0 to t dt. So, this expression this model actually provides the relationship between the radius of the particles as a function of time so now integrating, we can find out what is the time that is taken for reaching a certain radius.

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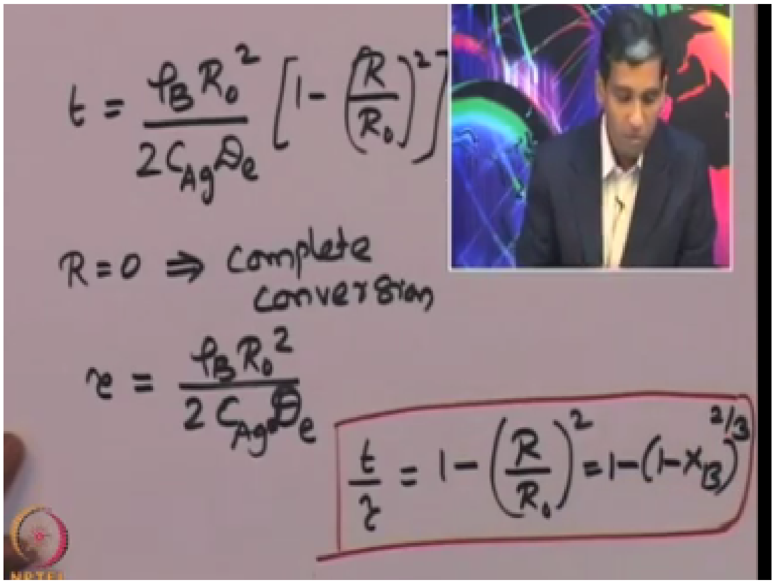

$$t = \frac{\rho_B R_0^2}{2 C_{Ag} \mathcal{D}_e}\left[1-\left(\frac{R}{R_0}\right)^2\right]$$

$R = 0 \Rightarrow$ complete conversion

$$\tau = \frac{\rho_B R_0^2}{2 C_{Ag} \mathcal{D}_e}$$

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

So time, t is given by Rho B R0 square / 2 times CAg* De effective diffusivity to 1 – R/R0 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 means all of the power all of the solids present in the particle has actually been completely consumed which means that R = 0 corresponds to complete conversation.

So under these conditions we can find out that the time taken for a complete conversion is given by Rho B R0 square / 2CAg * De which is the diffusivity of the particle a diffusivity of the species through the particle and so the fractional time that is taken to reach a certain radius of the unreacted core is essentially given by 1/1 – R/ R0 square that = 1 – 1 – XB to the power of 2/3 so this expression can be obtained.

Simply by taking the ratio of these two 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- conversion to the power of 2/3 now if we compare what is the corresponding expression in the case of the particles where the size of the particle does not change then it is a completely different expression and that is actually a given by.

In the case of constant size if we compare, we will see that if the film diffusion is controlling then in the case of constant size.

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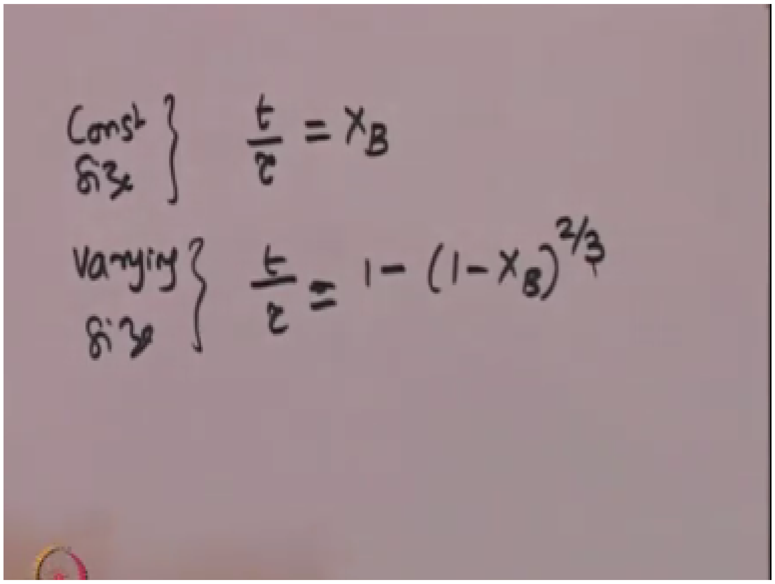

$$\left.\begin{matrix}\text{Const} \\ \text{size}\end{matrix}\right\} \quad \frac{t}{\tau} = X_B$$

$$\left.\begin{matrix}\text{Varying} \\ \text{size}\end{matrix}\right\} \quad \frac{t}{\tau} = 1 - (1 - X_B)^{2/3}$$

The fractional time that is taken = the conversion itself and while t/tau is actually given by 1 – 1-Xp power of 2/3, it is important to note that 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 sizes actually, particle is actually shrinking because of the reaction so what we have seen in todays 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 a different processes that may be controlling the overall reaction so this, we have done for 2 different cases 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.