

Chemical Reaction Engineering - II
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Lecture – 45
Fluid-Solid Non-Catalytic Reactions III

Friends let us summarize what we have learnt in the last lecture. The last lecture we initiated discussion on the fluid solid non-catalytic heterogeneous reactions and we looked at what are the different modes based on the nature of the catalyst nature of the non-catalytic hydrogenous 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 mode of heterogeneous reaction can be different and the resistances that are actually involved are different and we also described initiated two different types of models one is the progressive model a progressive conversion model. The other one is a shrinking core model and then we looked at because most of the reactions follow the shrinking core model.

We initiated the writing the writing balances to capture the size of the particle as a function of time for the shrinking core model. So, let us and also we discussed on different different processes which may maybe rate controlling and then let us continue from there. So, suppose if diffusion through the gas film controls the overall conversion.

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Diffusion through
gas-film Controlling

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

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

Suppose 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 particle core and that leads to formation of certain products and if we assume that the diffusion through the gas film is controlling which means that the concentration gradient is essentially in the gas film and as all the other processes.

There 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 the reaction that occurs at the interface of the ash layer and the unreacted core if that is also very fast.

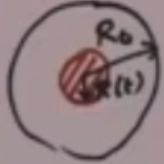
Then means that the concentration in ash layer and in unreacted core of species is approximately 0. So, which means that the in the timescales where the diffusion of the species occurs these the concentration in the ash layer and unreacted core of the species is approximately 0.

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

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

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

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


Now 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 soil reaction is given by $r^2 \frac{dr}{dt} = -k_g$ which is the mass transfer coefficient into the external surface area * the concentration of the species in the gas phase / 4π * density of the catalyst the density of the solid which is participating in the heterogeneous reaction not catalyst.

So, now the external we are we have assumed that it is a spherical particle. So, therefore as $S_{external} = 4\pi r_0^2$ where r_0 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 $r^2 \frac{dr}{dt} = -k_g C_{Ag} R_0^2 / \rho_B$. 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_0 and R remember that R is the suppose if this is the particle and the unreacted core is actually present at the centre and the R_0 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_0 and R .

Which will tell us what is the speed at which or what is the what is the radius as a function of time. So, $r^2 \frac{dr}{dt} = -k_g C_{Ag} R_0^2 / \rho_B$. 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.

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The image shows a whiteboard with handwritten mathematical equations. At the top, the equation is $\frac{1}{3} [R^3 - R_0^3] = -k_g R_0^2 C_{Ag} t / 4\pi \rho_B$. Below this, the equation is rearranged to $t = \frac{\rho_B R_0}{3 k_g C_{Ag}} \left[1 - \left(\frac{R}{R_0} \right)^3 \right]$. A note says "For complete conversion $\Rightarrow R=0$ ". A boxed equation defines $\tau = \frac{\rho_B R_0}{3 k_g C_{Ag}}$. To the right, the ratio $\frac{t}{\tau} = 1 - \left(\frac{R}{R_0} \right)^3$ is written.

And time is given by $\frac{1}{3} R^3 - R_0^3$ that is $= -k_g R_0^2$ 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 $C_{Ag} \times \text{time}$. So, that is the expression for the radius as a function of time. Now so we can rearrange this expression and we can find that time taken for reaching a certain under certain core radius is given by divided by R/R_0 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 been consumed for reaction to form the necessary products. So, for complete conversion complete conversion $R=0$ that is the radius of the reactor core has to be 0 which means that all of the solid which is available as reactant is now consumed.

So, suppose if τ is the time taken for complete conversion so far this expression setting $R=0$ we can find out the $\tau = \frac{\rho_B R_0}{3 k_g C_{Ag}}$. 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/by the time taken for the complete conversion.

So, that is given by $1 - R/R_0$ cube and that is essentially obtained by taking a ratio of this expression and this expression. So, if we take a ratio of these two expressions we will find what is the what is the time what is the time fractional time taken in order to reach a particular radius R . So, now if we define that the fraction of.

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The image shows a handwritten derivation on a whiteboard. At the top, it says "Frac unreacted". Below that, the equation is written as:

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

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

Below this, an arrow points to a boxed equation:

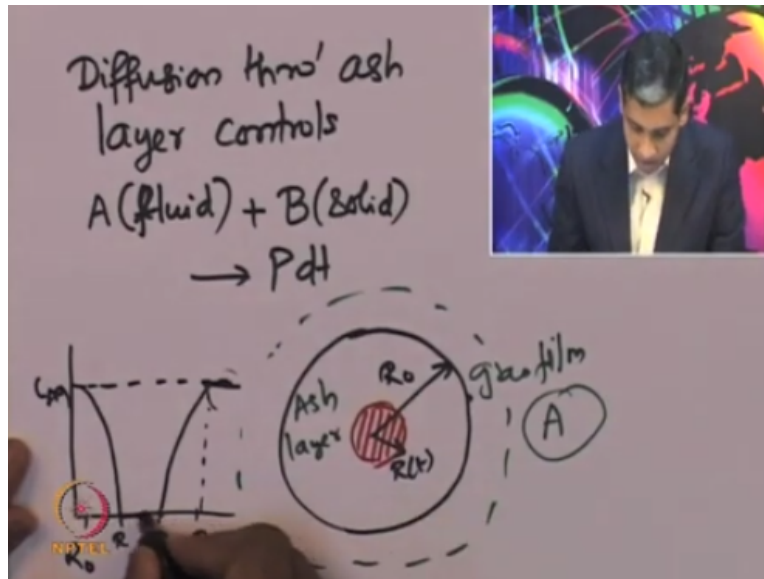
$$\Rightarrow \frac{t}{\tau} = X_B = 1 - \left(\frac{R}{R_0}\right)^3$$

Fraction unreacted what is the fraction of the core which is unreacted then that is given by $1 - X_B$ if X_B is the conversion of the solid B represents the species present in the solid and that is = volume of unreacted core / the total volume of the particles total volume of the particles. So, that is given by $4/3/R^3$ where R is the instantaneous radius of the unreacted core and $4/3 * \pi R_0^3$ where R_0 is the radius of the initial particle.

So, that is given by R/R_0 the whole cube so therefore from this relationship between the conversion and the instantaneous radius of the unreacted core we can rewrite the fractional read it the time taken to reach a particular radius as T/τ = the actual conversion and that is = $1 - R/R_0$ 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.

So, next if we look at the diffusion through the ash layer suppose if we look at diffusion through ash layer.

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So, both if we assume that the diffusion through the ash layer that is the layer which is present between the unreacted core and the gas film. So, the species from bulk a there 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 aware the reaction occurs. So, suppose if the diffusion through the ash layer is actually the current rate controlling step is that is the slowest step.

On the other two that is the reaction step and the diffusion through the gas film if these two are actually very fast steps compared to the diffusion through the ash layer. Then we can now monitor the system as you make that the diffusion 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 and species B in solid form leads to the formation of products.

It must be noted here that the stoichiometric coefficient of B can take values other than 1 and we can now suppose if R_0 is the initial. Suppose R_0 is the initial radius of the spherical particle spherical particle which is actually participating in the in the in the heterogeneous reaction and suppose if there is a unreacted course and the instantaneous radius of the unreacted core let us say this has given by R of T .

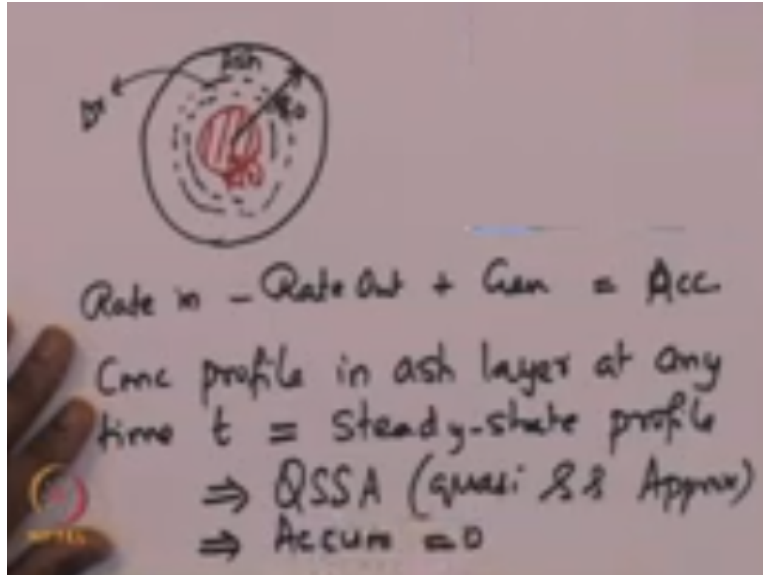
So, that is a function of time and there is a gas film which is actually present around this particle so the gas film is present around this particle. So, the species A diffuses from gas film from the bulk to the gas film to the surface of the particle and then diffuses through the ash layer. So, this is the ash layer and diffuses through the ash layer. So, therefore we expect that if diffusion through the ash layer is the controlling step.

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 our R_0 that is the radius of particle and this is the centre of the of the sphere and this is R_0 and if this is R that is the instantaneous radius of the unreacted core.

Then we can expect that the quantity if suppose this is the that 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 were in the bulk in the bulk gas phase and in the gas film in the concentration essentially remains as the concentration as that of the bulk concentration which is C_{Ag} or C_{A0} and there will be a gradient of this species A 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 and so the concentration of species in the unreacted core is going to be 0.

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Now we can write a simple mole balance in order to capture the rate of change of the concentration of the 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 respect radius of the unreacted core changes with time. So, let us write a simple mole balance suppose this is the entry this is the initial particle.

Suppose if this is the particle at any time T and the radius of the particle is R₀ remember that it is there until the size of this particle is not changing. And if the un reacted 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 if we take a small element and the thickness of this element is delta R and if we assume that the positive R.

The radius of the radius going outward from the centre is the positive direction then we can write we can write a mole balance where we can say that the rate at which the species is entering this element -the rate at which the species leaves + whatever is being generated that should be=0 that should be equal to accumulation sorry. So, now if we assume that the if you assume that the concentration profile in the ash layer.

So, this was the ash layer here so if you assume that the concentration profile in ash layer at any time is =the steady state profile which means that if you 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 =0 s if we assume quasi steady state this means that there is no accumulation.

So, accumulation is =0 so therefore we can now write a mole balance where the rate at which the species enters if W_{Ar} is the molar flux that at which the species is entering that element ΔR thickness at R .

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

$$\Rightarrow \lim_{\Delta r \rightarrow 0}$$

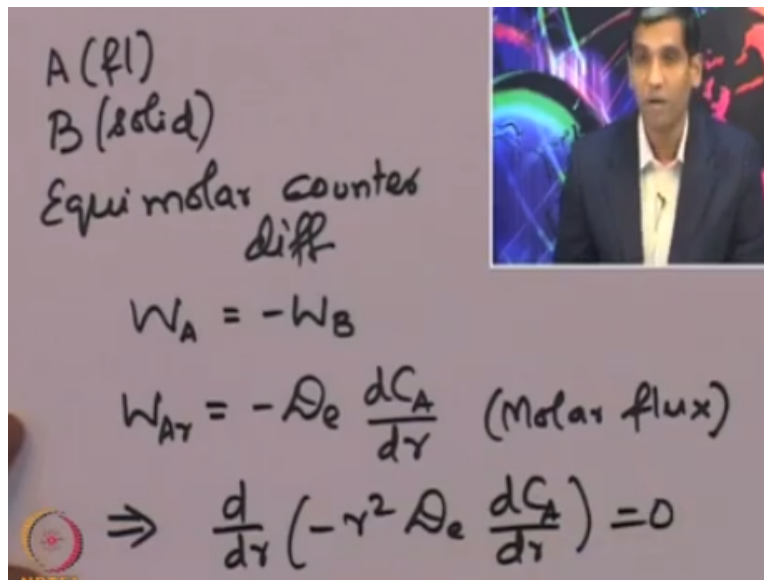
$$\Rightarrow \boxed{\frac{d}{dr} (W_{Ar} r^2) = 0}$$

So, that W_{Ar} at r is the molar flux with which the species is entering that element $4\pi r^2$ it is a molar flux but the balance is written in molar rate square. W_{Ar} which is the molar flux*the corresponding area at r and $W_{Ar} * 4\pi [r^2 + r + dr]$ that is the rate molar rate at which the species enters these element this is the molar rate with a species leaves+ 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 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 Δr goes to 0 so then we will get the model equation will reduce to $\frac{d}{dr} W_{Ar} * R^2 = 0$. So, that is the okay that is the mole balance that is the that is the mole balance.

Now we need to know what is this W_A . W_A is the molar rate and the process with which the species is actually entering that element is the diffusion. So, the molar flux can actually be related to the concentration using the Fick's law. And suppose if we assume that it is an equal molar counter diffusion. So, because there are two species which is participating in the reaction species A which is in the fluid phase and species B which is the solid phase.

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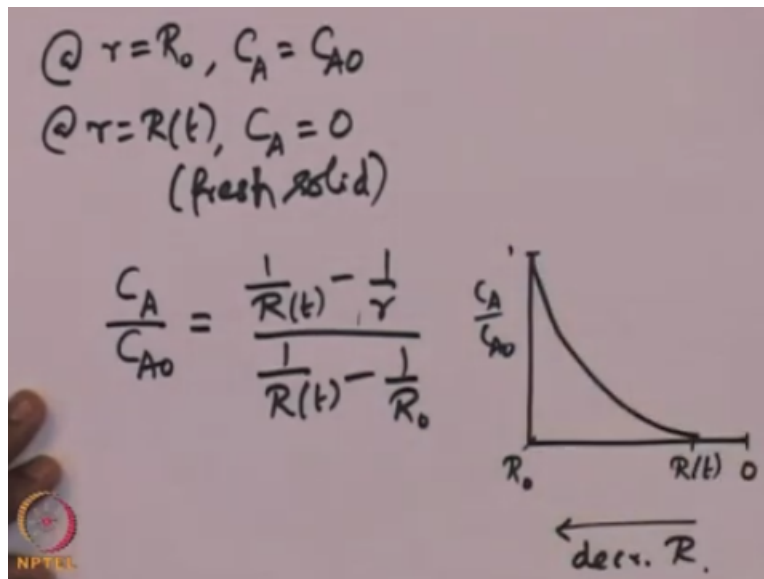
$A(\text{fl})$
 $B(\text{solid})$
 Equimolar counter diff
 $W_A = -W_B$
 $W_{A,r} = -D_e \frac{dC_A}{dr}$ (Molar flux)
 $\Rightarrow \frac{d}{dr} (-r^2 D_e \frac{dC_A}{dr}) = 0$

So, suppose if we assume that if you assume that if it is equimolar counter diffusion if you assume equimolar counter diffusion from stoichiometry we can actually discern that the flux with which the species A is actually entering B = the flux with which the species B is actually reacting to form a certain product. So, therefore W_A is given by $-D_e$ which is the effective diffusivity of the species $\cdot dc/dr$ and so plugging the molar flux.

So, this is the flux assuming that it's equimolar counter diffusion that is the molar flux and D is the corresponding diffusivity and plugging this into the mole balance we find that the mole balance is $dC_A/dr - R = 0$ so deep by dr minus r^2 . 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 quasi steady state for the concentration profile in the ash layer.

That is the instantaneous concentration can be assumed to be that of the steady state profile in the ash layer. So, the corresponding boundary conditions are.

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At $R=R_0$ which is the outer rim of the particle remember that the particle size does not change so at $R=R_0$ we expect that the concentration of the species is =that of the bulk concentration or the gas phase bulk concentration and at $R= R$ of T which is now remember the radius is now changing with time. Because the unreacted core is now shrinking so $C_A=0$ because this is a diffusion layer ash layer diffusion controlled process.

And because I know also at $R=T$ there is a that are fresh solid is present the 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 C_A/C_{A0} that is $=1/R$ which is basically which is a function of time- $1/R/1/r-1/R_0$. So, $1/e$ is any position between R_0 and R and R of T is the location of the unreacted core.

And R_0 is the outer rim of the particle so now if I sketch the sketch the concentration profile so if this is the centre of the sphere and this is R_0 . So, that is the thickness of the sphere so this is decreasing R and let us say this is R of T of the unreacted core is actually present between 0 and R of T . So, if we plot C_A/C_{A0} then the concentration profile essentially it looks like this. So it decreases from 1 all the way to 0 at R of T because the reaction actually occurs since quickly at this location.

Now in order to obtain the rate in order to obtain the in order to find out what is the radius of the unreacted core.

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Find $R(t)$
Molar flux at
fl-solid interface

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

Balance on elemental solid

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 find out from because its diffusion control the molar flux at the interface the molar flux at fluid solid interface where the reaction actually occurs. Because we have assumed that its diffusion controlled in the ash layer so as soon as the fluid species reaches the surface of the of these of the unreacted core the reaction is going to occur immediately.

So, the molar flux at the fluid solid interface should be =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 W_{Ar} which is =the diffusivity $D \cdot dC_A/dr$ at $r=R$ and that is given by $-D_e C_{A0}/R^2 \cdot (1/R - 1/R_0)$. Now because the reaction occurs immediately the rate which the 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 on the elemental solid we can write a balance on elemental solid in order to relate the rate of reaction and flux.

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$$\begin{aligned}
 \text{Rate in} - \text{Rate out} + \text{Gen} &= \text{Acc Rate} \\
 = 0 \quad = 0 \quad + r_B'' 4\pi R^2 &= \frac{d(\phi_B \rho_B V)}{dt} \\
 &\quad \downarrow \\
 &\quad \text{Vol. frac} \\
 &\quad \text{of solid} \\
 \Rightarrow r_B'' 4\pi R^2 &= \frac{d}{dt} \left(\phi_B \rho_B \frac{4}{3} \pi R^3 \right) \\
 \Rightarrow \frac{dR}{dt} &= \frac{r_B''}{\phi_B \rho_B}
 \end{aligned}$$

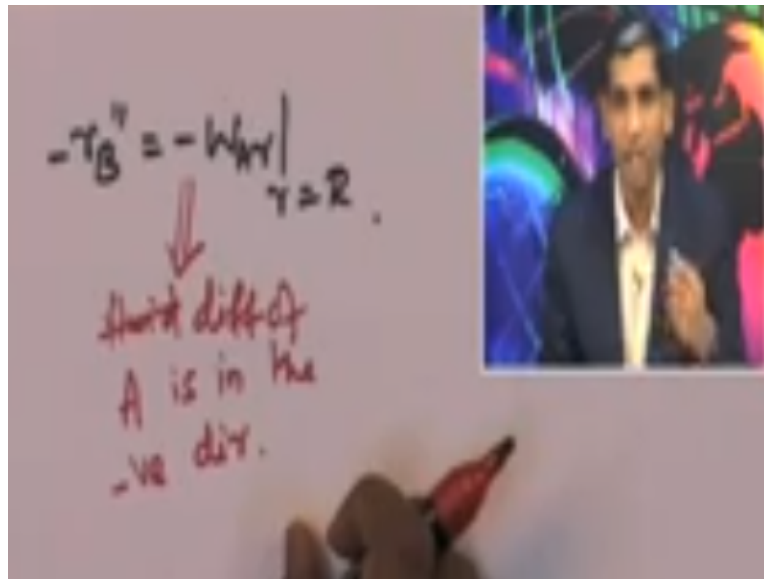
So, the rate at which this solid that actually enters in the ash layer which is =0- the rate at which the solid leaves the ash layer that is =0 and the rate at which it is being generated is basically the r_B'' is the reaction rate multiplied by the area of the unreacted core. Because the action actually is occurring on the surface of the unreacted core and the solids are not moving. So, for the rate in and 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/dt of $\phi_B \rho_B V$ the volume of the particle. Now ϕ_B is nothing but the volume fraction 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 $r_B'' 4\pi R^2$ that is $=d/dt \pi R^3$.

On simplifying this expression we will find that dr/dt which is the rate at which the unreacted core radius changes with time and that is equal to divided by $\phi_B \rho_B$. So, now because it is the diffusion controlled in the ash layer soon after the 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 of the unreacted core.

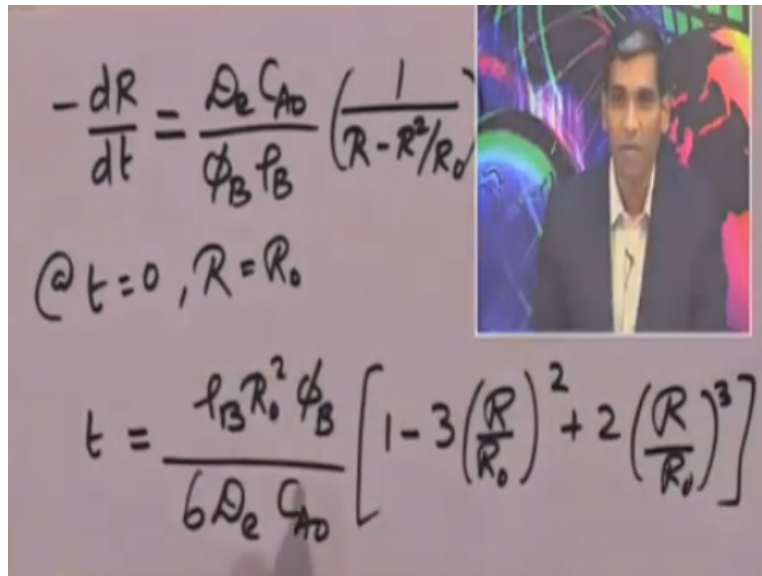
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So, therefore $R_B = -W_A r$ at $r=R$ so remember that the - sign here is essentially refers to the fact that the fluid because the diffusion of species the fluid diffusion the diffusion of species A is in the negative direction. So, we said that the sign convention is we assume that the outward direction is positive and the diffusion of this species A is actually going from outside to the inside of the particle.

So, therefore the diffusion is actually in the negative R direction and that is why there is a -sign that has been inserted here and that should be $=De C_{A0}/R^2 * (1/R - 1/R_0)$. So, this expression relates the rate at which the solid is being consumed for reaction and the other properties of that system. So, from here we can find out the we can rewrite the expression for dr/dt .

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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=R₀

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

Which is the rate at which the radius changes with time that is $=1/R - R^2/R_0$. So, now we can integrate this expression at time $t=0$ that is when the reaction has not started then the size of the unreacted core is $=R_0$ and so we can integrate this expression and we can find out that the time taken to reach a certain radius of the unreacted core is given by $\rho_B R_0^2 \phi_B$ which is the volume fraction of the unreacted core which is occupied by the solid $/6 * \text{diffusivity} * C_{A0}$.

Multiplied by $1 - 3 (R/R_0)^2 + 2 (R/R_0)^3$. 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 the of the system.