Chemical Reaction Engineering - II
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Lecture – 44
Fluid-Solid Non-Catalytic Reactions II

So next let us look at the shrinking core model.

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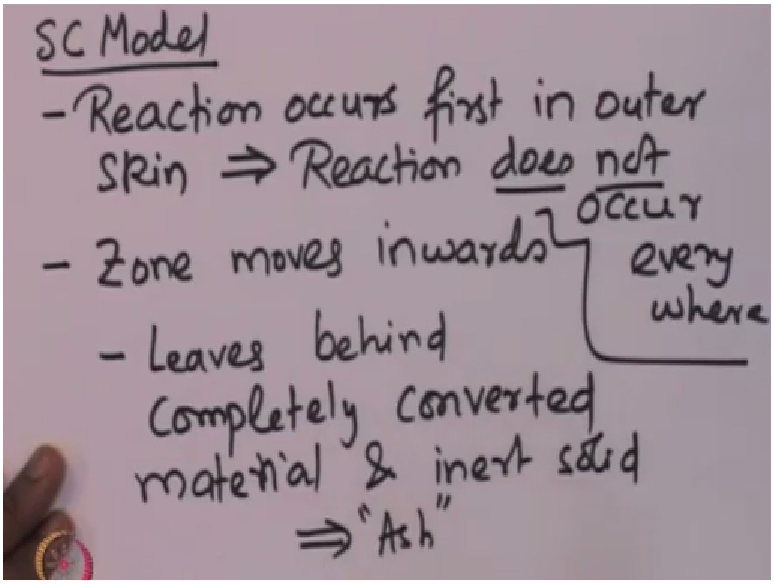

SC Model

- Reaction occurs first in outer skin ⇒ Reaction does not occur every where
- Zone moves inwards
  - Leaves behind completely converted material & inert solid ⇒ "Ash"

So the shrinking core model assumes that the reaction first occurs in the outer skin and then it assumes that the reaction zone actually moves inwards. So the first assumption also means that the reaction does not occur everywhere in the solid core unlike what was assumed in the progressive conversion model and it also because the reaction first occurs in the outer skin, the reaction zone actually starts moving inward as the reaction proceeds.

And then once it moves inwards, as the reaction zone moves inside what it does is, it leaves behind the completely converted material and also some of the inert solids which may already be present in the solid core. So the converted products are now assumed that it sticks back into the solid core and whatever inert solid which is unreacted they also will stick back in the solid core.

And so these 2 together is termed as ash, so the ash in the solid core is basically a combination of the products which are actually completely converted material and also the inert solids which would have not reacted in the reaction. So these 2 are called as ash products. Now if we attempt to depict the concentration profiles. If you attempt to intuit what is the concentration profile in the solid core. If we assume a shrinking core model is essentially it looks like this.

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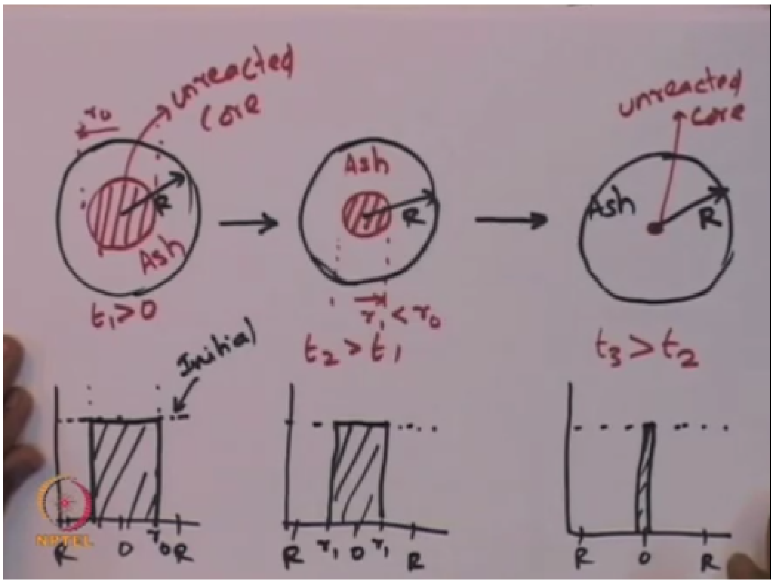

Suppose if this is the solid core and let us say at some time as the reaction is started at some times if this is the unreacted core, remember that the shrinking core model assumes the reaction first occurs at the outer skin and then the reaction front starts moving towards the inwards of the solid core. So which means that at any time there will always be a small unreacted core until the conversion is complete which means that all the solid has been consumed.

So till all the solids have been consumed there will always be some location where the unreacted solids are present. So let us say at some time t1, which is > 0. So this is the, there is some amount of unreacted core which is present and the outside layer is called the ash layer. Now as time proceeds then the scenario will be if this is the solid core which was started initially and the reaction has started.

This is the initial size of the solid core, so now the unreacted core will start shrinking in size because the reaction front has started moving towards the center of the solid particle and there will be again ash which is present outside this. So the radius of this unreacted core if I call this r1. So this r1 will be smaller than the radius of the unreacted core which was presented in earlier time.

So this is r0, small r0, so if that radius will be smaller than this r0, which means that the reaction front has moved inside and the solid which is present between r0 and r1 has now reacted to form products. So this is at let us say time t2 which is greater than t1 and at a later time, so if this is the original size of the solid core, in which the reaction was started then the unreacted core will now reduce to a very small size until it completely disappears.

So this is the unreacted core and everything outside is basically ash now where it is pretty much converted and this might be at a later time t3, which is greater than t2. So now if we look at the concentration profile for this situation. So if this is 0, so at this time the solids are present only in this unreacted core, so therefore the concentration of the solids will essentially be the concentration of the solids which was present initially everywhere.

However, it is present only, so this is the initial concentration of the solids then at this particular time t1 the solids are present only in this location between 0 and r0; however, the concentration will be as much as the initial concentration itself and then at the next time step, so the region where the unreacted solids are present is now going to shrink; however, the concentration in that location will continue to remain as that of the initial concentration.

Then if I once again plot at a much later time this particular, this region will start shrinking. So this is at 0, so 0 is the center of the sphere and so the unreacted solids are now present only in this very small region which is around the center of this particular sphere, if you assume that the solid core in which the reaction is started is actually a spherical particle.

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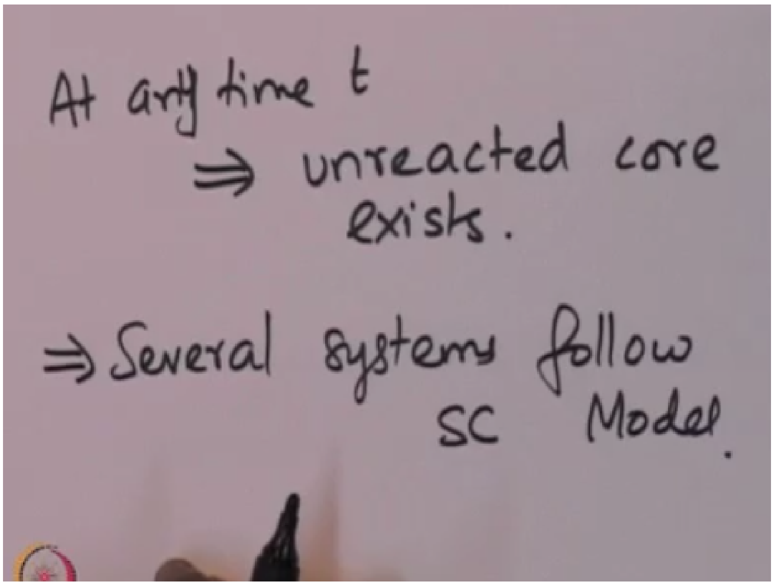

At any time t

⇒ unreacted core exists.

⇒ Several systems follow SC Model.

So what is model assumes that at any time there always exist at any time unreacted core always exists. So this might be very small or very big, but at any time there is always unreacted core that exists. So now there have been experiments that have been performed where the catalyst particle, where the solid core after the reaction has occurred which is again a non-catalytic reaction has actually been cut open to check the extent of carbon that has been consumed.

So if it is a carbonaceous reaction after some, certain conversion at different times the carbon can actually be cut open and then looked at what is the extent of consumption of carbonaceous material towards forming the corresponding product. So it has been observed that for that several systems actually follow this shrinking core model. So now so let us look a little bit more deep into what exactly happens in the shrinking core model because it is actually very relevant that many systems actually follow a shrinking core model.

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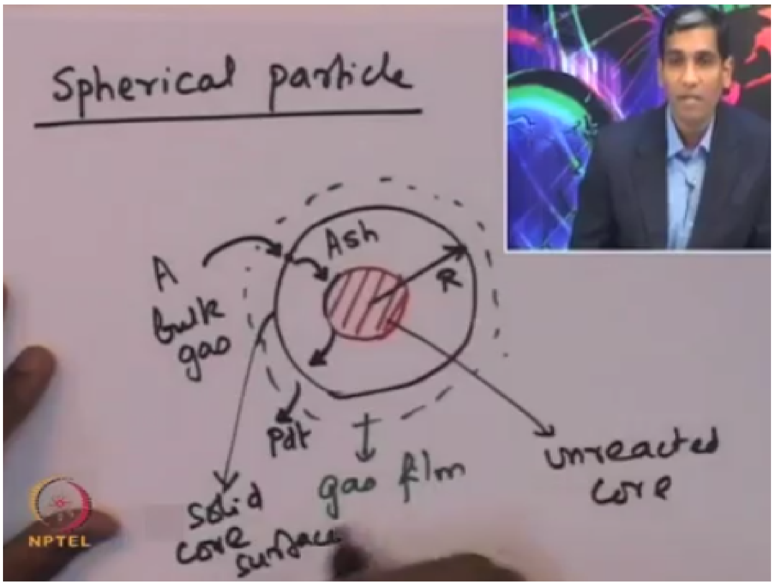

Suppose if we assume that it is a spherical particle then if this is the initial core. So let us say that there is a spherical particle and of radius R. So that is the initial core that was actually started with and let us assume that the unreacted core is actually present somewhere here. So it is again concentric with the, let us assume that it is concentric with the periphery of the spherical particle.

And then if we assume that there is a gas which is present outside then there will be a small gas film, so this gas film will exist around the spherical particle and the gas which is present in the bulk, so let us say this is bulk gas stream, this is bulk and this is the ash layer and this is the unreacted core. So if species A, let us say if this is the species A is present in the gas stream.

So the species A now first has to go into the gas fill and then it has to go into the surface of solid-core. So this is the solid-core surface. So A has to now diffuse into the surface of this solid core and then it has to diffuse through the ash layer and it has to reach the unreacted core. So it has to reach the location of the unreacted core. Remember that in this ash region there is no solid reactant which is present and therefore no reaction is happening in the ash layer.

So the reaction actually happens only at the periphery of this unreacted core. The moment the reaction occurs the product which is formed has now has to diffuse through the ash layer and then it has to diffuse from the ash layer into the gas stream, gas film and then to the bulk gas so let us say that this is the product. So the diffusion of the product. So once the bulk species diffuses through the ash and then it reaches the surface of the unreacted core the product is formed and then the diffusion occurs and then the product leaves the spherical particle.

So this is the scheme that actually occurs in the, this is how the, this is the process that describes the transfer of reactants into the solid core and then the occurrence of the reaction in the unreacted core and the transport of the products back into the gas stream in the shrinking core type model. So clearly there are 3 processes which are actually occurring.

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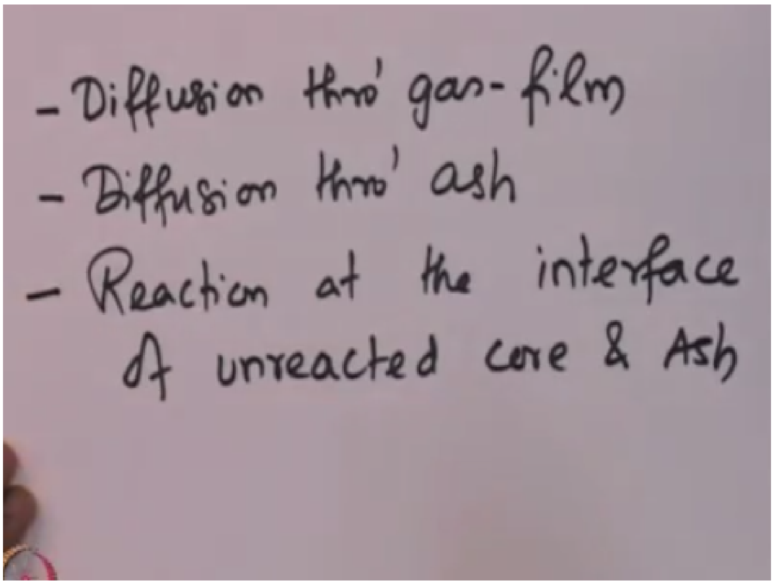

- Diffusion thro' gas-film
- Diffusion thro' ash
- Reaction at the interface of unreacted core & Ash

So the first process is diffusion through gas film and then the second process is diffusion through ash and the third process is reaction at the interface of unreacted core and ash. So therefore the extent of reaction that is the overall conversion of the reactant, of the solid depends upon which of these 3 processes a rate limiting step. So it could be that the diffusion through the gas film is an extremely slow step.

So remember that the rate limiting step is essentially the one which is the slowest step and because it is the slower step it controls the actual reaction which is occurring in the, it controls the overall conversion. So suppose if the diffusion of the gas from the bulk to the surface of the core through the gas film if that is an extremely slow process, when can it be slow?

If the diffusivity, if the effective diffusivity of the species through the gas stream to reach the surface of the solid core if that is extremely small, if the diffusivity is very low then that can in principle serve as a rate controlling step. Now particularly when the reaction is faster than the diffusion step. Now the second possibility is where the diffusion through the ash. So there is an unreacted core and there is ash which is surrounding the unreacted core.

So the reactants have to now diffuse from the surface of the core through the ash and it has to reach the location where the unreacted core is present. So let me repeat the reactants have to actually diffuse from the periphery of the solid particle through the ash and it has to reach the surface of the unreacted core. So if that diffusion of this reactant species through the ash layer, if that is very slow then that can in principle be a limiting step.

Now the third possibility is where the reaction which is occurring at the periphery of the unreacted core. So if that is an extremely slow if the specific reaction constant is small then it can principle actually be controlling and all the other processes can actually be faster. So essentially there are 3 possibilities where.

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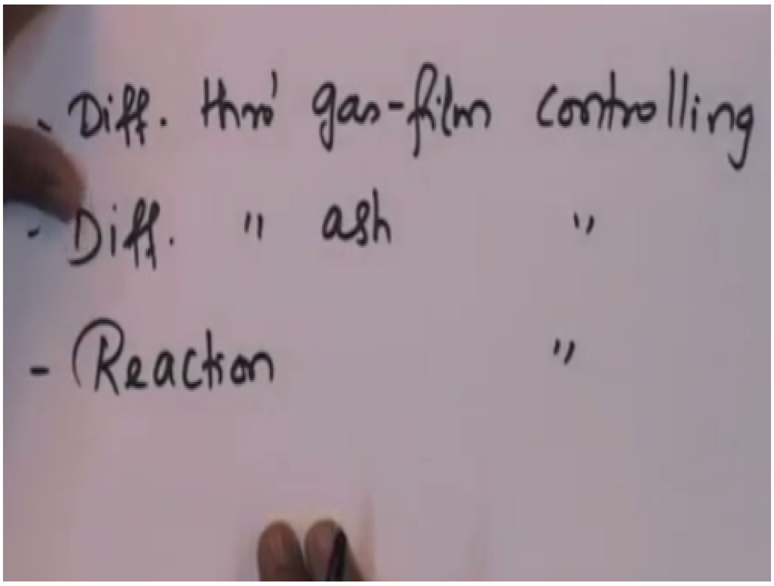

- Diff. thro' gas-film controlling
- Diff. " ash "
- Reaction "

So it could be diffusion controlling, diffusion through ash layer controlling or reaction controlling. So let us try to model the system if the rate controlling step is doing any of these 3.

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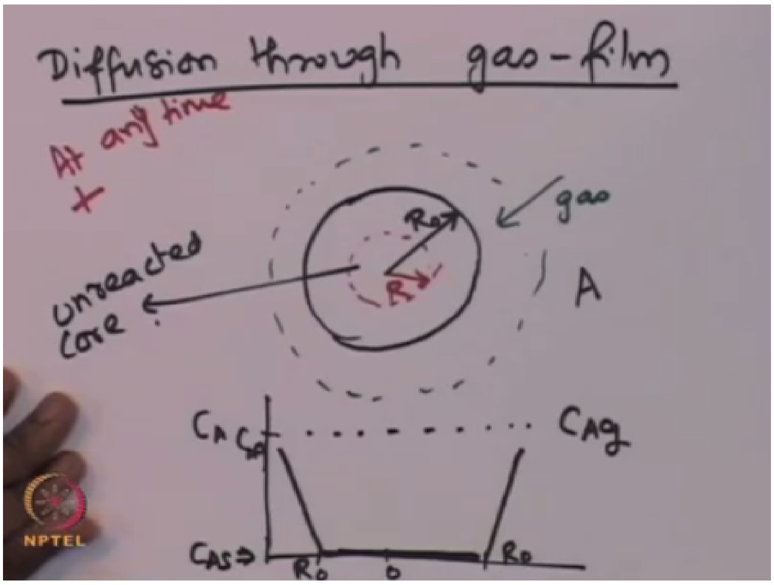

Diffusion through gas-film

So let us start with the first one, where we assume that the diffusion through gas film is the controlling step. Let us assume that diffusion through gas film is rate controlling. Now what happens here, suppose if this is the original particle with which the reaction was initiated and if the radius of this particle is let us say R and if the unreacted core let us say at, so let us say that the initial radius is R0 and the unreacted core, the radius of the unreacted core which is depicted in red color here if that is R.

So that is the at any time t, so the radius of the unreacted core is now R and the original radius of the particle in which the reaction was initiated is R0. Let us assume that there is a gas phase which is actually present around it. So this is the gas phase and this is the unreacted core. Now if we attempt to intuit what is going to be the concentration profile of let us say species A which is in the gaseous form and it now diffuses through to actually react with the solid in this particle.

So let us now try to intuit what is going to be the concentration of the species. So suppose if this is the concentration of species A, then because we assume that diffusion through the gas film is controlling, the diffusion process in the gas film is going to be much slower than the other 2 processes which is actually occurring inside the solid core. So therefore we expect that there will be a concentration.

Suppose if this is the bulk concentration, CAg is the bulk concentration of species A, then if this, we can expect that there will be a concentration gradient in the gas film. So this is at the center of the, that is the center of the core and this is R0, that is R0 and again this is R0. So we can expect that there will be concentration gradient outside the core and there will be no concentration gradient inside the core.

And this is because as soon as the gas species actually enters the core the reactant A will be immediately consumed because it is a very fast process compared to the diffusion rate, rate of diffusion of species A to the surface of the catalyst. So the concentration of the species inside the core is expected to be 0. So that is the concentration inside the of the surface and also the concentration of the species inside the core.

So now if we know this then how do we attempt to characterize this. So if we need to understand the dynamics of the concentration change for this system, we need to start with the mole balance. So suppose if the diffusion through the gas film is basically the limiting step then the driving force,

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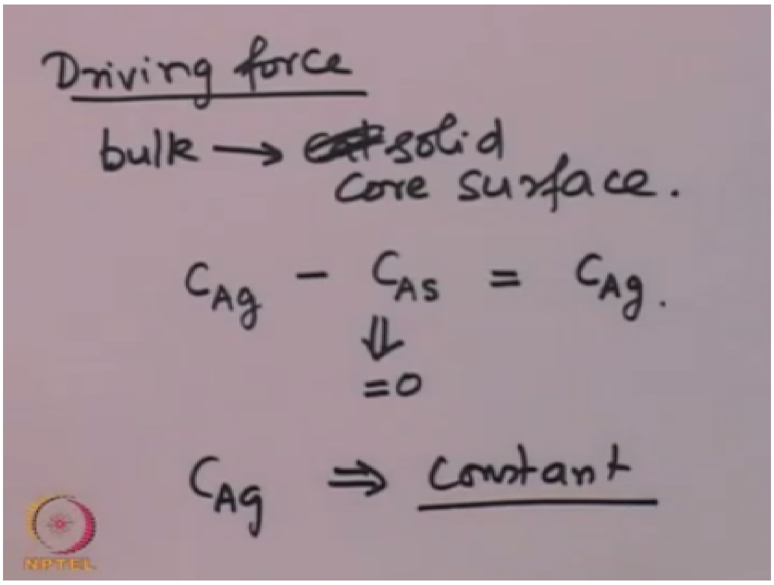

Driving force

bulk → ~~cat~~ solid core surface.

$$C_{Ag} - \underset{\underset{=0}{\Downarrow}}{C_{AS}} = C_{Ag}.$$

$$C_{Ag} \Rightarrow \underline{\text{constant}}$$

The driving force for the species to get transported from the bulk to catalyst surface, the core surface of the solid core not catalyst that will be essentially be C Ag, which is the concentration of the species in the bulk gas - the concentration of the species in the surface, but we know that because the reaction and the diffusion through the ash layer is faster compared to the diffusion of the species through the gas phase, C As is actually expected to be 0.

So therefore the driving force is essentially the concentration of the species in the gas phase itself. Now suppose if we assume that the gas phase bulk concentration is constant. Suppose if we assume that this is constant, it is reasonable because in a real system we may be able to feed the gas at a certain rate in order to maintain a constant concentration of that particular species in the gas phase. So with this we can actually write a simple mole balance.

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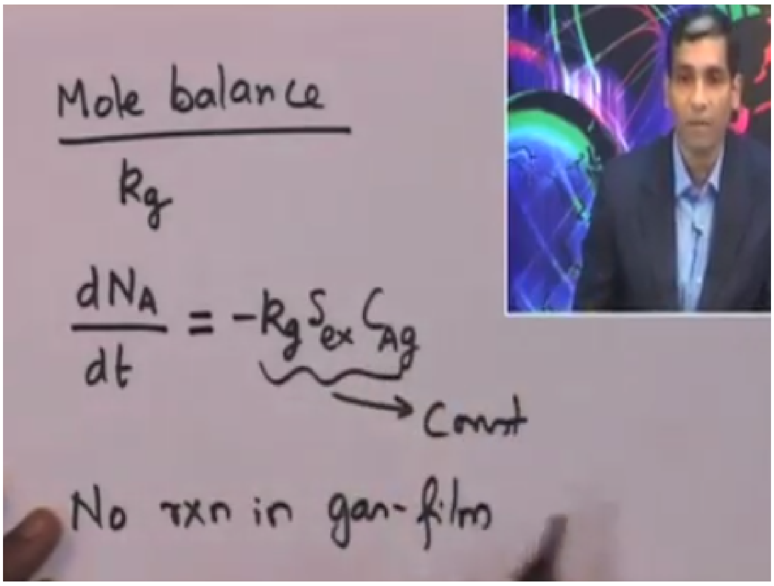

Mole balance

k_g

$$\frac{dN_A}{dt} = -\underbrace{k_g S_{ex} C_{Ag}}_{\rightarrow \text{Const}}$$

No rxn in gas-film

Now the rate at which rate of change of the number of moles of species A with respect to time that should be = the rate at which the species is coming in – the rate at which the moles are going out + whatever is being generated. Now the only process which is actually occurring here is basically the transport of the species from the bulk onto the surface of the core.

So that is actually a mass transport process, so suppose if we define a mass transport coefficient kg then we can write the rate as dN A, so remember that A is the gas species which is actually moving from the bulk to the solid core where the reaction is occurring. So dN A/dt where N A is the number of moles of A which is actually defusing from the bulk to the surface of the core.

The reaction is occurring only inside the core and so there is no reaction in the gas phase. So there is no reaction in gas film. So the only process which actually controls the rate of change of number of moles in the gas phase is essentially the transport of species from the bulk to the surface of the solid core because of diffusion. So that should be = -kg, let us say that is the mass transport coefficient and typically the units are centimeters per second.

And if S external is the surface area of the core, external surface area of the core and that multiplied by the concentration of the species in the bulk phase. So that is the mole balance which captures the rate of change of number of moles of species A in the gas phase. Now because C Ag is constant we can assume that this whole expression is basically a constant. The ex is essentially the external surface area of the core and that is expected to be constant.

Because we assume that the particle size is not changing significantly and then kg is the mass transport coefficient, there are several correlations which are actually available in order to estimate what is the mass transport coefficient for transport of a particular species from a bulk phase to the surface of a solid core and CAG essentially can be maintained constant. So therefore the right-hand side of this balance is essentially a constant.

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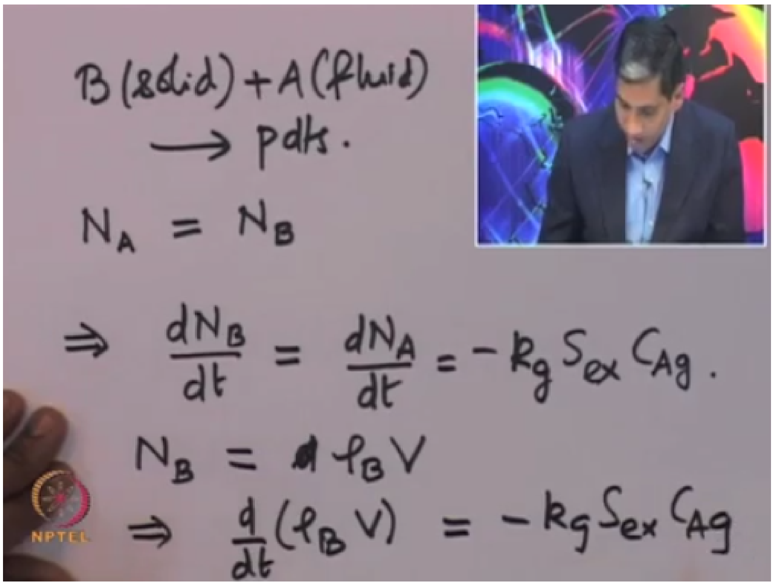

B (solid) + A (fluid)

$\longrightarrow$ pdk.

$N_A = N_B$

$$\Rightarrow \frac{dN_B}{dt} = \frac{dN_A}{dt} = -k_g S_{ex} C_{Ag} .$$

$N_B = \rho_B V$

$$\Rightarrow \frac{d}{dt}(\rho_B V) = -k_g S_{ex} C_{Ag}$$

So suppose we assume that B is a solid, which reacts with fluid A to form products, then we can assume that there is an equimolar consumption. Suppose if we assume that the B and A are basically under equimolar condition, the reaction is occurring under equimolar condition then the number of moles of A, which is consumed because of the reaction should be = the number of moles of B which is consumed because of the reaction.

Note that NA = NB is actually a special case and in general these 2 need not necessarily be equal. Now why do we need this because we need to now monitor either the, we can now monitor actually the amount of solid that is actually being consumed because of the reaction and that is what is of interest and this, the mole balance that was written for the gas species in the gas film can actually be used in order to estimate what is the number of moles of the solid reactant that was actually being consumed because of the reaction.

And this is in the case of this when the diffusion in the gas film is actually controlling the overall reaction. So therefore if NA is = NB, which is the number of moles of the solid that is being consumed in the reaction and from here we can rewrite the mole balance as d NB/dt =

DNA/dt and that is = -kg which is the mass transport coefficient * the external surface area * the concentration of the species A in the gas phase.

Now we know that the number of moles of the solid which is actually present in the solid is essentially given by the density of the species rho B * the volume and so we can rewrite this as d/dt rho B * volume that should be =, so the number of moles of solid which is present in the core can actually be related to the volume of the core using this expression NB = density of the solid which is present in the core * the volume of the core at any instant time t.

So remember that the volume changes as a function of time because as the reaction occurs the core is now shrinking and so the volume of the unreacted or volume of the unreacted solid core changes with time.

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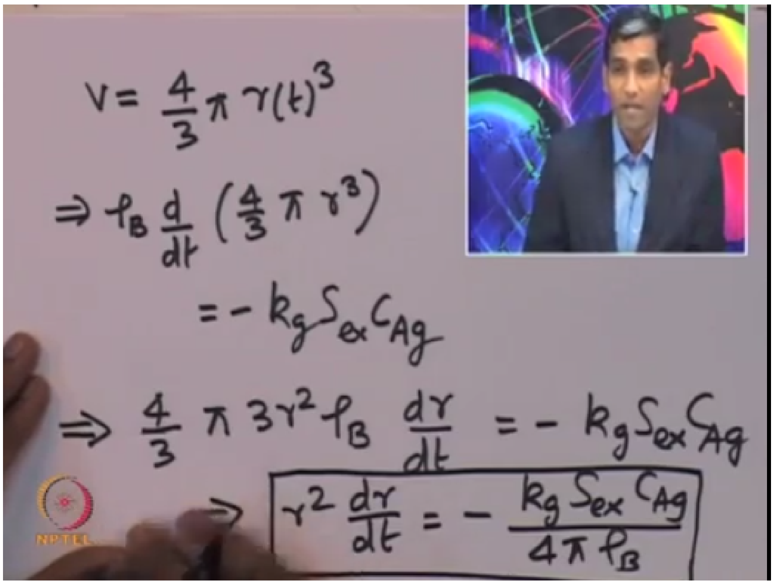

$$V = \frac{4}{3}\pi r(t)^3$$

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

$$= -k_g S_{ex} C_{Ag}$$

$$\Rightarrow \frac{4}{3}\pi 3r^2 \rho_B \frac{dr}{dt} = -k_g S_{ex} C_{Ag}$$

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

So if volume of because you assume that it is a spherical particle the volume is given by 4/3 pi r cube, so remember that this r is a function of time because as time progresses the core actually sinks in size and so the radius of the unreacted material is actually a function of time. So now if we plug in this expression the mole balance we will find that rho B d/dt 4/3 pi r cube.

r is the function of time that should be = -kg, which is the mass transport coefficient * the external surface area of the initial particle, spherical particle that was chosen * the bulk concentration of this reactant species A and so that can simply be rewritten as 4/3 pi 3 r square rho B dr/dt C Ag, that will be = r square dr/dt that is = - kg * C Ag/4 pi * rho B.

So that is the balance, so that describes how the radius of the unreacted core actually changes with time. Now this is directly correlated to the number of moles or the amount of solid that is actually undergoing a reaction that is the amount of solid that is actually undergone the reaction at a certain time. So now if at r = capital R, so the ash is now present.

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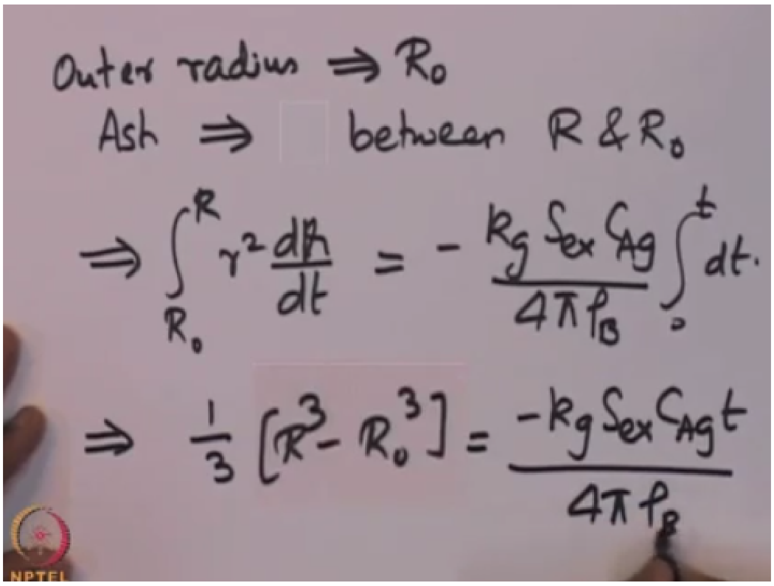

Outer radius ⇒ R_0

Ash ⇒ between R & R_0

$$\Rightarrow \int_{R_0}^{R} r^2 \frac{dR}{dt} = -\frac{k_g S_{ex} C_{Ag}}{4\pi\rho_B}\int_0^t dt.$$

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

So we assume that the outer radius of the core is R0 and if the ash is actually present, ash is present between R and R0, we can now integrate this expression between R0 and R dr/dt and that should be = -kg/rho B * integral t dt. So that is the, so now this actually, this integration will now provide an expression for finding what is the radius of the unreacted core as a function of time.

So integration suggests that it will be 1/3 that is =, * rho B, so this expression provide the relationship between the radius of the unreacted core as a function of time. So if the diffusion in the gas phase is actually controlling the overall reaction, overall conversion then we can find out how the unreacted core actually decreases in size as the reaction proceeds. So what we have seen in today's lecture is essentially introduction about the different, what is the fluid-solid non-catalytic system.

And what are the different modes based on the change in the size of the solid core that is participating in this fluid-solid non-catalytic heterogeneous reaction and then we looked at 2 different models the progressive conversion and the shrinking core model, a description of these 2 models and we have attempted to write a balance in order to find out what is the size of the unreacted solid core as a function of time for a shrinking core model when the diffusion in the gas phase is actually controlling. Thank you.