Chemical Reaction Engineering II

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Lecture - 29

Fluid solid non catalytic reactions III

Friends, it is a good time to summarize what we have learnt in the last couple of lectures. So, we looking at the fluid solid hydrogenous non catalytic hydrogenous reactions and then we identified 2 possible cases 2 possible modes: One is situation where the particle which is actually participating in the reaction it does not shrink with as reaction progresses and then other situation where the particle which participates in the reaction actually shrinks in size as the reaction progresses And then we look at 2 possible model progressive convention model and the shrinking core models and it was observed that the shrinking core models is more common in most of the situations.

So, we developed models for the shrinking core model for both the particle size unchanging particle size and also for those particle which were shrinking in size. And that for situation where the overall reaction over all conversation actually controlled by different rate controlling steps. For example, the diffusion of the gas base form the bulk through the gas film to the surface of the core and all the diffusion of the species through the ash layer or it is see reaction controlling. So, the expression that we get for the time that is taken for the unreacted cor to reach a certain size, which is directly core related with the conversation of the solid species can be summarized as below.

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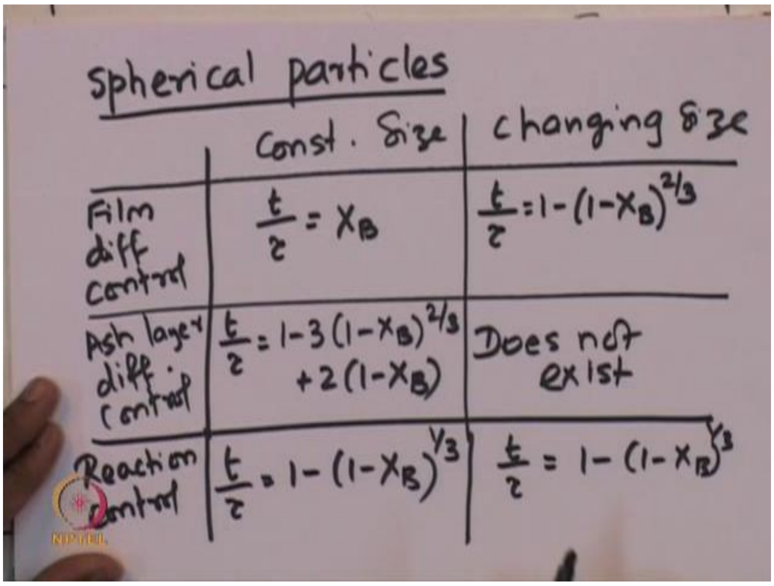

Spherical particles

	Const. Size	changing size
Film diff control	$\frac{t}{\tau} = X_B$	$\frac{t}{\tau} = 1-(1-X_B)^{2/3}$
Ash layer diff. control	$\frac{t}{\tau} = 1-3(1-X_B)^{2/3} + 2(1-X_B)$	Does not exist
Reaction control	$\frac{t}{\tau} = 1-(1-X_B)^{1/3}$	$\frac{t}{\tau} = 1-(1-X_B)^{1/3}$

So, 1st spherical particles so, it can be summarized in this table here. So, for spherical particle suppose we take the constant size and varying or changing size there are 2 possible modes. Here, changing size refers to the special case know ash lay present. As noted in the earlier lecture the size can change even if the ash layer present use densities soiled product and the reaction are different. Now, suppose if it is gas film diffusion control if the overall reaction is controlled by the film diffusion control. Then we found that t by tau where t is a time taken for the unreacted core to reach certain radius, because of the hydrogenous reaction. That should be equal to the conversion of the solid itself which is directly related to the amount of solid that is reacted.

Then in changing size the same makes expression for the same would be t by tau is 1 by 1 minus 1 minus x b to 2 the power of 2 by 3. Here, tau is the time taken for the complete conversion that is all of the solids which is presented in the code s is gone for the complete reaction. Now, next possibility is ash layer control ash layer ash layer diffusion control. So, if ash layer diffusion is controlled in the overall conversion in that case t by tau is given by 1 minus 3 into 1 minus xB to the power of 2 by 3 plus 2 into 1 minus xB. So, that is the expression for t by tau and of course, in changing size the ash layer does not exist and therefore, it does not offer any resistors to the overall conversion.

Then the third case is where the reaction is controlling the overall conversion is if there is the reaction control, then t by tow is given by 1 minus 1 minus xB to the power of 1 by 3 and t by tau is given by 1 minus into 1 minus xB to the power of 1 by 3. In both cases the time taken for the un reacted code to reaches the radius the depends on the conversion in exactly the same way, because the presence or absence of the film or the ash layer does not contribute to the overall conversion if it is in reaction control region.

Now, all this we look for spherical particles what happens if it is a other geometry, for example: there is a plating of metals then normally it is not plated on spherical particle it is plated on other kinds of geometrics; it could be a cylindrical geometry or could be a flat plate geometry or it could be any other coverage.

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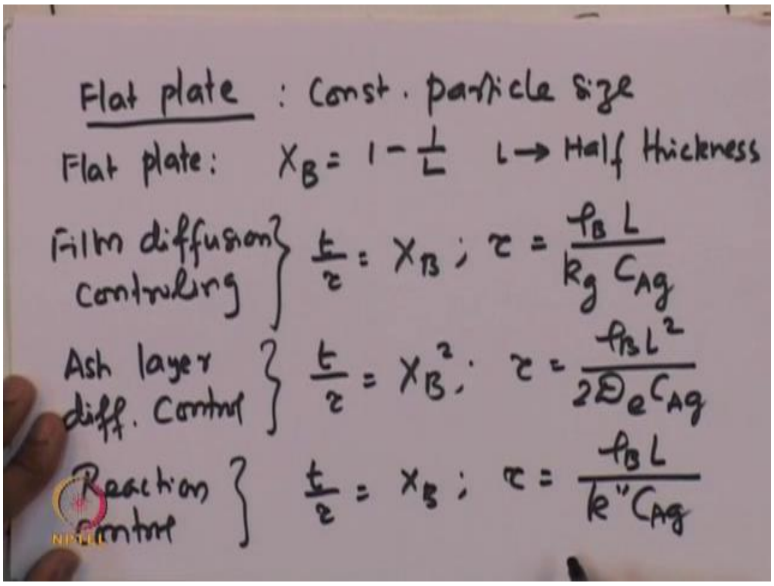

Flat plate : Const. particle size

Flat plate: $X_B = 1 - \frac{l}{L}$ l → Half thickness

Film diffusion controlling } $\frac{t}{\tau} = X_B$; $\tau = \frac{\rho_B L}{k_g C_{Ag}}$

Ash layer diff. Control } $\frac{t}{\tau} = X_B^2$; $\tau = \frac{\rho_B L^2}{2 \mathcal{D}_e C_{Ag}}$

Reaction control } $\frac{t}{\tau} = X_B$; $\tau = \frac{\rho_B L}{k'' C_{Ag}}$

So, let us look at 2 specific other geometries which are fairly common 1 is flat plate. Suppose, if it is a flat plate where the solid is now present in the flat plate there is a fluid which is now coming on to the surface of the flat plate and the hydrogenous reaction is occurring at the surface of the flat plate. So, in that case, if we consider the constant particle size if we consider the constant particle size. Then if the for a flat plate 1 can actually define 1 can define conversion as 1 minus 1 by L where, L is essentially half thickness of the plate that is actually being used for used as a solid reaction.

If the if it is a film diffusion controlling as regime in that case t by tau is given by xB where tau is given by tau is the time taken for the total conversion; that is for all the solids to undergo reaction. That will be given by the density of the particle divided by in to the half thickness length scale divided by into mass transport coefficient into concentration of this species in the gas face. If it is ash layer diffusion control then t by tau is essentially given by xB square and where tau is given by row B L square divided by 2, diffusivity into concentration of the species in the gas face.

If it is reaction control then t by tau is simply given by xB and tau is given by row B L divided by k double prime which is the in centric rate cost multiplied by CAg. K double prime is the in centric specific rate and CAg is the corresponding gas face concentration. Now, similar expressions have been obtained for cylinder geometry they are as follows in this table.

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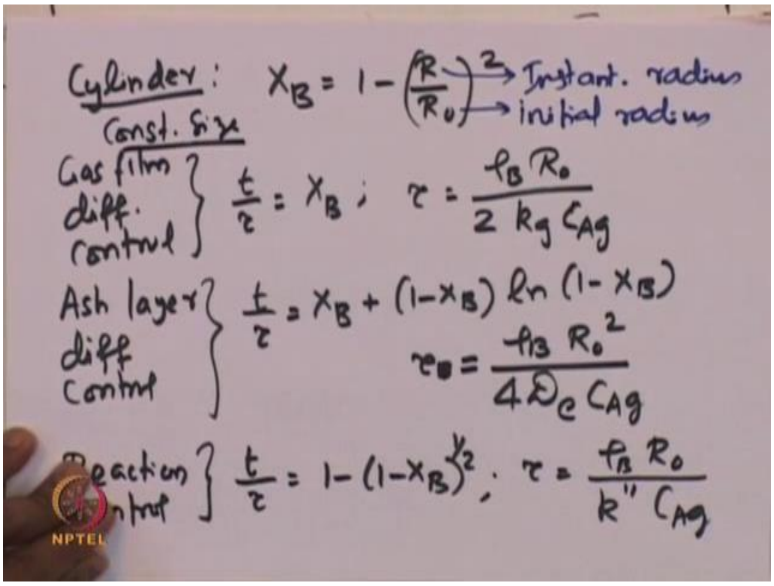

Cylinder: $X_B = 1 - \left(\frac{R}{R_0}\right)^2$ R → Instant. radius, R_0 → initial radius

Const. size

Gas film diff. control } $\frac{t}{\tau} = X_B$; $\tau = \frac{\rho_B R_0}{2 k_g C_{Ag}}$

Ash layer diff control } $\frac{t}{\tau} = X_B + (1 - X_B) \ln (1 - X_B)$

$\tau_B = \frac{\rho_B R_0^2}{4 \mathcal{D}_e C_{Ag}}$

Reaction control } $\frac{t}{\tau} = 1 - (1 - X_B)^{1/2}$; $\tau = \frac{\rho_B R_0}{k'' C_{Ag}}$

So, for cylinder for a cylindrical geometry the xB conversion of the solid is defined as 1 1 minus R by R not t whole square. Now, here r not is the initial radius of the R not is the initial radius initial radius of the cylinder and R is the instantaneous radius of the cylinder. So, with definition if we if it is gas face diffusion control gas film if it is gas film diffusion control, then t by tau is essentially given as xB and tau is equal to row B into R not which is the initial radius divided by 2 times k g into CAg.

So, that is the time taken by the core for complete conversion and if it is ash layer diffusion control then t by tau is given by xB plus 1 minus xB multiplied by the natural logarithm of 1 minus x b. Where, tau is tau b tau is time for total conversion that is given by row B into R not square divided by 4 De into CAg.

So, that is the concentration of the species at the gas face and if it is reaction control the t by tau is essentially given by 1 minus 1 minus xB to the power of half and tow is equal to row B into R not divided by k double prime; that is the specific reaction rate multiplied by CAg. So, this sort of summarizes the various time taken for the core to reach a certain radius, if the overall reaction is controlled by different resistances which is actually available in the system. So, all these have for basically constant size system.

Similar expressions can actually be worked out or varying size as well. So far looked at the cases where the overall reaction is actually controlled by resistors one of these 3 resistances which are available. That is either the diffusion through the gas film or the diffusion through the ash layer in the case of constant particle size and or if it is a reaction control. So, the in reality this is not the situation. In reality what happens is that all 3 resistances actually contribute.

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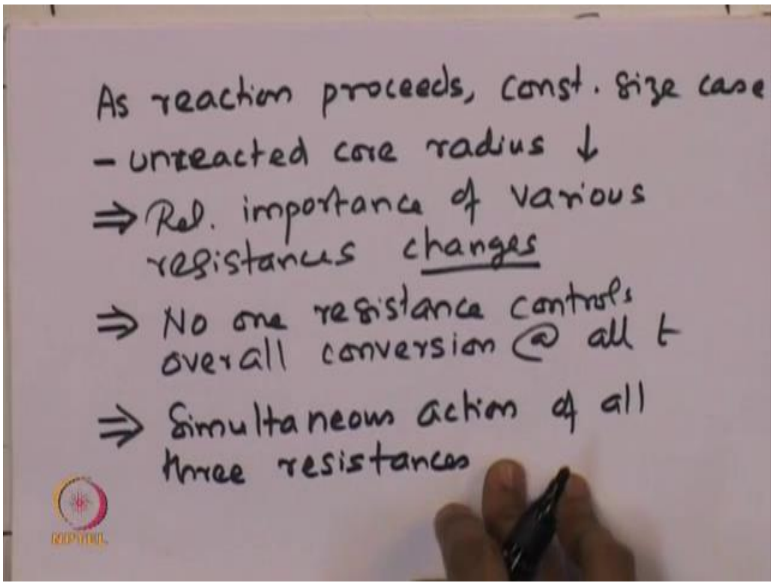

As reaction proceeds, const. size case

- unreacted core radius ↓

⇒ Rel. importance of various resistances changes

⇒ No one resistance controls overall conversion @ all t

⇒ Simultaneous action of all three resistances

So, as reaction proceeds the in facts are true because as reaction proceeds even in the constant size case even in the constant size case. What is observed is that the of course,, the unreacted course core radius is going to decrease; unreacted core radius decreases as the reactions proceeds. And therefore, as a result the relative importance of various resistances is going to change. That is very important; because there are 3 resistances as the size of the unreacted core changes then the relative importance of these different resistances towards their effect on the overall conversion also is going to change. So, which means that not 1. So, no 1 resistance controls over all conversion all times all time t.

So, therefore, it is important to simultaneous consider simultaneous action of all the resistances. So, it is important to consider simultaneous action of all 3 resistances. So, if you want to incorporate all 3 resistances, then the model for the radius of the unreacted core as a function of time that the differential equation; which basically tells what is the rate of relates the rate of the change of the radius of the unreacted core. With respect to time to all the other properties and concentrations of the system can actually be rewritten by using a using a combination of all the resistances.

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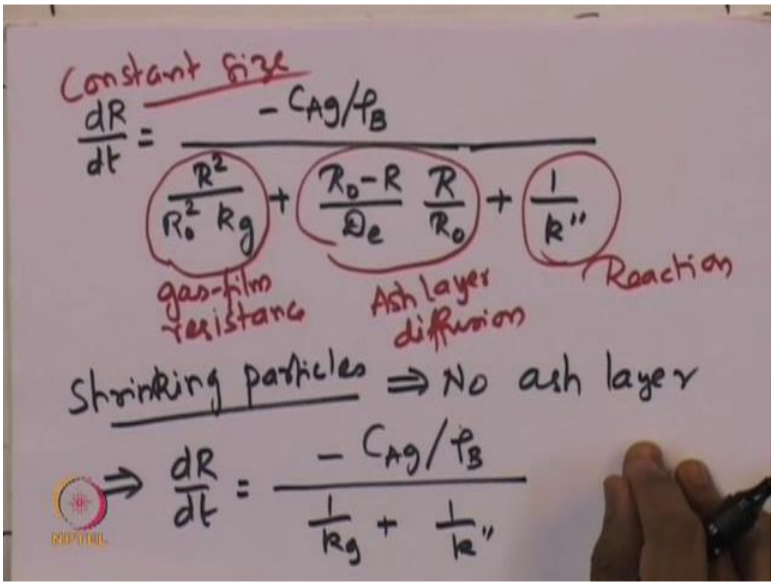

Constant size

$$\frac{dR}{dt} = \frac{-C_{Ag}/\rho_B}{\frac{R^2}{R_0^2 k_g} + \frac{R_0-R}{\mathcal{D}_e}\frac{R}{R_0} + \frac{1}{k''}}$$

gas-film resistance

Ash layer diffusion

Reaction

Shrinking particles ⇒ No ash layer

$$\Rightarrow \frac{dR}{dt} = \frac{-C_{Ag}/\rho_B}{\frac{1}{k_g} + \frac{1}{k''}}$$

The rewritten model will be dR by dt there will be equal to minusCAg divided by row B. CAg is the gas face concentration row B is the density of the solid that is used divided by R square by R not square into k g plus R R not minus R divided by the diffusivity into R by R not plus 1 by k double prime. That is the specific reaction rate. Now, here it is assume that the volume fraction of the solid in the unreacted core is approximately equal to 1. So, they are 3 terms here which correspond to 3 different resistances. So, the 1st 1 here this correspond to the gas film resistance.

This corresponds the ash layer this correspondence the diffusion in ash layer and last time correspondence to the reaction resistance; resistance, due to the heterogeneous reaction that is occurring in the on the on the surface of the unreacted core. So, now, suppose this is for a constant size system if the particle size does not change this is for the constant size system. Suppose, if there is consider same think can be return for a shrinking core shrinking size type of particles, where there is no ash layer.

So, if there is no ash layer then the resistance due to ash layer does not exist. So, simply we can obtain the expression by removing the resistant due to the ash layer which represents the expression here. So, for shrinking particles there is no ash layer. So, therefore, we can write this expression as dR by dt is minus CAg by row B divided by 1 by k g plus 1 by k double prime. Where, k double prime is the specific rate and k g is the corresponding mass transport coefficient.

So, now, let us take an example problem and see how we can predict the dissolution of a particle of certain type which is undergoing such kind of a fluid solid; non catalytic hydrogenous reaction. An excellent example of that is the drugs which are actually being administered. So, the solid drugs which are administered for curing a certain disease they when they going into the body they have to dissolve and it is important to understand how much time does it takes for the for the drug which is a solid particle to dissolve.

That dosage of the drug actually strongly depends on the time taken for the complete resolution. So, therefore, it is important to model days from the pharmacokinetics stand point of view.

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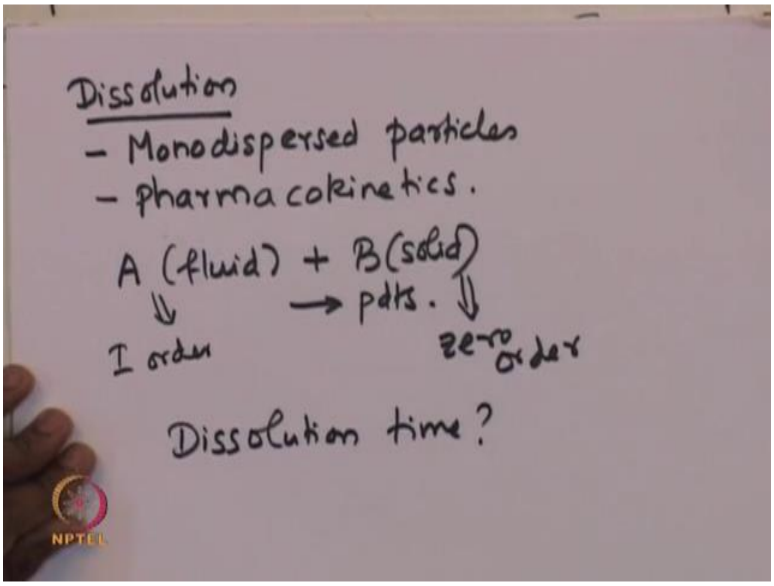

Dissolution

- Monodispersed particles
- pharmacokinetics.

$$\underset{\text{I order}}{\underset{\Downarrow}{A\,(\text{fluid})}} + \underset{\text{zero order}}{\underset{\Downarrow}{B\,(\text{solid})}} \longrightarrow \text{pdts.}$$

Dissolution time?

So, let us look at this problem. So, dissolution of a solid particles suppose if you assume that there are all these drugs which are given inside; they are all mono dispersed particles. That is all the particles that are actually in the drug or size this is not true always,, but let us assume to start with that, all particles are actually same size that is it is a mono dispersed system. And then, so this is … So, we need to the objective is to find out what is a dissolution time which actually plays an important role in the pharmacokinetics. Now, suppose if there is a species A which is basically in the fluid stream that react with certain solid, which is essentially the drug particle.

That leads to formation of products. Now, if we assume that the fluid a actually reacts with the core which is which contains the solid material. And we assume there is 1st order with respect to the fluid the reaction rate is 1st order with respect to fluid and 0 order with respect to the solid which is present. Then the question is what is the dissolution time. So, need to estimate the objective of problem is to find the dis dissolution time; the time that is taken for the dissolution of these particles.

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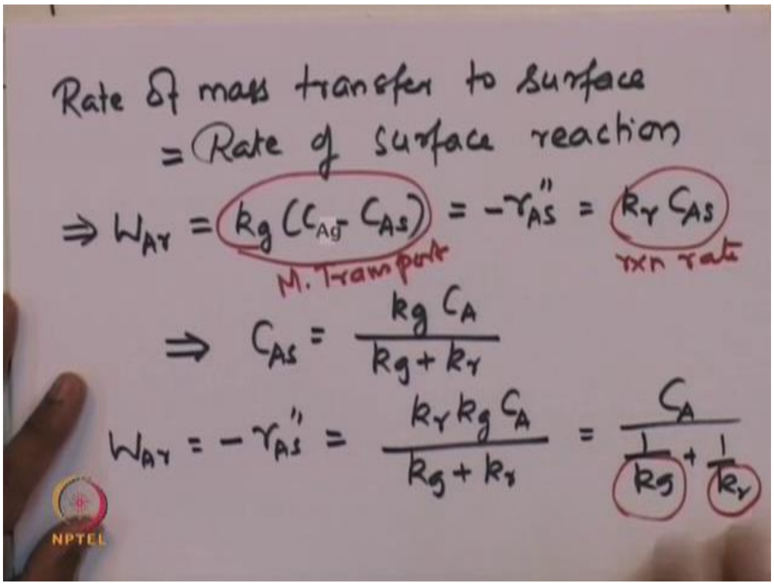

Rate of mass transfer to surface

= Rate of surface reaction

$$\Rightarrow W_{Ar} = \underbrace{\boxed{k_g (C_{Ag} - C_{As})}}_{\text{M. Transport}} = -r''_{As} = \underbrace{\boxed{k_r C_{As}}}_{\text{rxn rate}}$$

$$\Rightarrow C_{As} = \frac{k_g C_A}{k_g + k_r}$$

$$W_{Ar} = -r''_{As} = \frac{k_r k_g C_A}{k_g + k_r} = \frac{C_A}{\frac{1}{\boxed{k_g}} + \frac{1}{\boxed{k_r}}}$$

So, now, we can observe we can we can actually the rate of the mass transport to the surface is actually equal to the rate of surface reaction. Why is this? Because the particles are expected to as the properties of drugs are always such that the particles are expected to dissolve. So, there the particle this is actually the process where the particles are actually shrinking in size. So, there is no ash layer which is actually present. So, therefore, the rate of mass transport to the surface should be equal to the rate at which it is being consumed for the surface reaction.

So, therefore, we can write the WAr if there is t flux at which the species actually travelling from the bulk gas trace to the surface of the solid. That is equal to kg CA minus CAS, where CA is the bulk concentration and CAs is the surface of a surface concentration. And that should be equal to the reaction rate rAS double prime and that is equal to kr is the specific reaction constant multiplied by CAS.

So, that is the surface concentration and this is the net reaction rate. So, this the reaction rate and this the mass transport this correspondence to the mass transport. So, from here we can actually eliminate CAS. So, note that ca s is the quantity which cannot be actually measured experimentally,, but CA is the bulk concentration in that can actually be measured. So, we need to be eliminate CAS which is not a measurable property measurable quantity. So, k g into c a divided by k g plus kr. So, plugging in this back into the expression for WAr we find that double prime that is equal to kr kg CA divided by kr and that is equal to CA by 1 by kg plus 1 by kr.

So, therefore, if we know the mass transport coefficient and the and the reaction in specific reaction rate, then we will be able to actually calculate the required quantities which are the dissolution time. So, therefore, now there is a need to find out what is mass transport coefficient. So, you can use core relation in order to find the mass transport mass transport coefficient kg.

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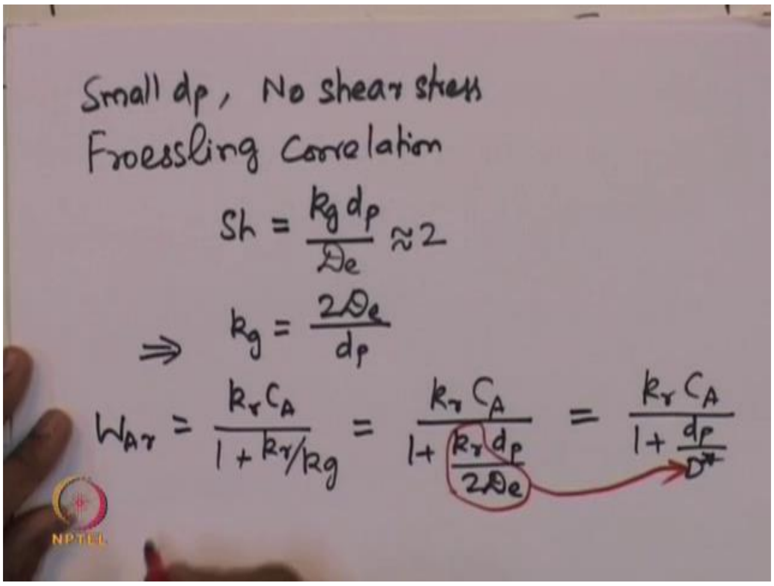

Small dp, No shear stress

Froessling Correlation

$$Sh = \frac{k_g d_p}{\mathcal{D}_e} \approx 2$$

$$\Rightarrow k_g = \frac{2\mathcal{D}_e}{d_p}$$

$$W_{Ar} = \frac{k_r C_A}{1 + k_r/k_g} = \frac{k_r C_A}{1 + \frac{k_r d_p}{2\mathcal{D}_e}} = \frac{k_r C_A}{1 + \frac{d_p}{D^*}}$$

So, suppose if we assume that the particles are small under dp and if there is no shear stress at the boundary of the fluid and solid then we can actually using Froessling correlation. You can find out that Froessling correlation we can find out that Sherwood number which is equal to the mass transport coefficient into diameter of the particle divided by the corresponding, that is approximately is equal to 2.

So, from here we can find out that the mass transport coefficient is given by 2 time diffusivity divided by the corresponding particle diameter of the particles which is actually being dissolved. So, plugging back into the expression for flux we find the WAr equal to kr into CA 1 plus kr by kg and that is equal to kr into CA divided by 1 plus kr into dp divided by 2 times Definitions. And which can be rewritten as kr into CA divided by 1 plus dp by D star.

So, where D star is nothing but the ratio of 2 times De into kr that want D star. So, the D star or the meaning of the D star is that basically tells you the diameter at which the mass transport and reaction rate actually equal.

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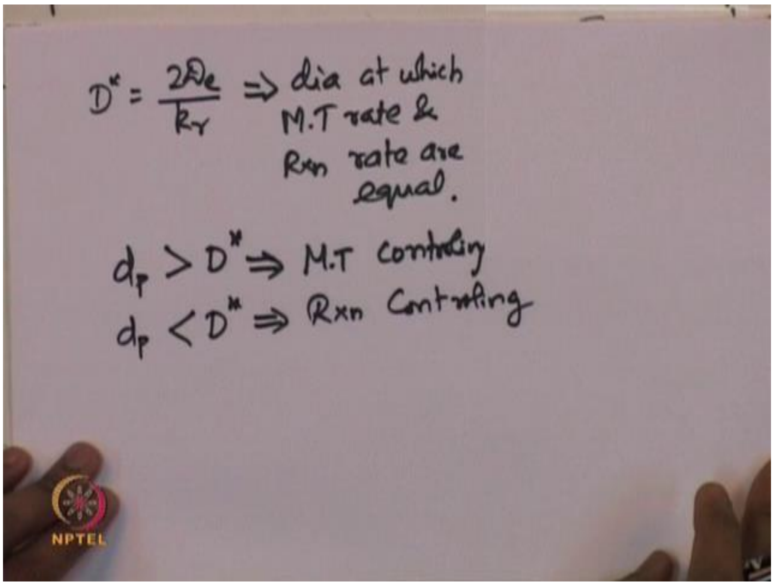

$D^* = \frac{2\mathcal{D}_e}{k_r} \Rightarrow$ dia at which M.T rate & Rxn rate are equal.

$d_p > D^* \Rightarrow$ M.T controlling

$d_p < D^* \Rightarrow$ Rxn Controlling

So, if we look at what is the expression for D star, D star is 2 time de divided by kr and that is the that essentially the diameter at which the mass transport rate and the reaction rate are equal reaction rate are equal. So, therefore, if the diameter of the particles if larger than D star, then it can be expected that it is mass transport controlling.

While if the particle diameter is less than d star then it is actually expected to be a reaction controlling scheme the overall conversion is expected to be a reaction controlling. So, now, in order to find the radius of the particles as a function of time we can write a mote balance on the solid particles.

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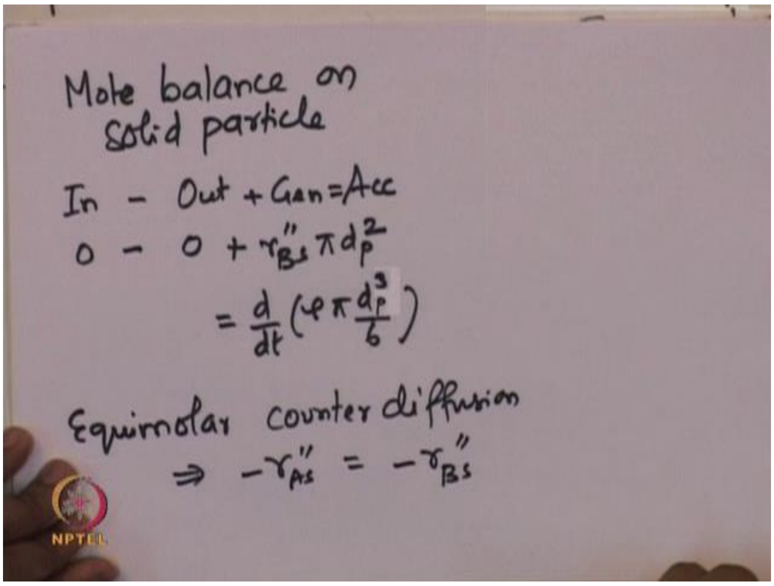

Mole balance on solid particle

In − Out + Gen = Acc

$$0 - 0 + r''_{Bs} \pi d_p^2 = \frac{d}{dt}\left(\rho \pi \frac{d_p^3}{6}\right)$$

Equimolar counter diffusion

$$\Rightarrow -r''_{As} = -r''_{Bs}$$

The mole balance goes as here, mole balance on solid particles. So, where whatever at which things are coming inside minus whatever rate at which the particles are leaving out plus generation should be equal to accumulation, that is the balance. Now, nothing is coming inside because it is the solid which is actually participating. So, there is no flow. So, nothing is coming inside and nothing is actually leaving.

But some of it actually being reacted,. So, that is the generation term if rBS is the rate at which the solid is being consumed at the surface of the particle multiplied by pi into dp square that is the surface area of the solid particle. And that should be equal to d by d t into density into volume of the spherical part. So, suppose if you assume equimolar counter diffusion, then the minus rAS double prime that is the rate at which A is actually being consumes, because of the hydrogen reaction. That should be equal to minus rBS rate at which the solid is been consumed. This is because of the diffusion and which is associated with the particular reaction.

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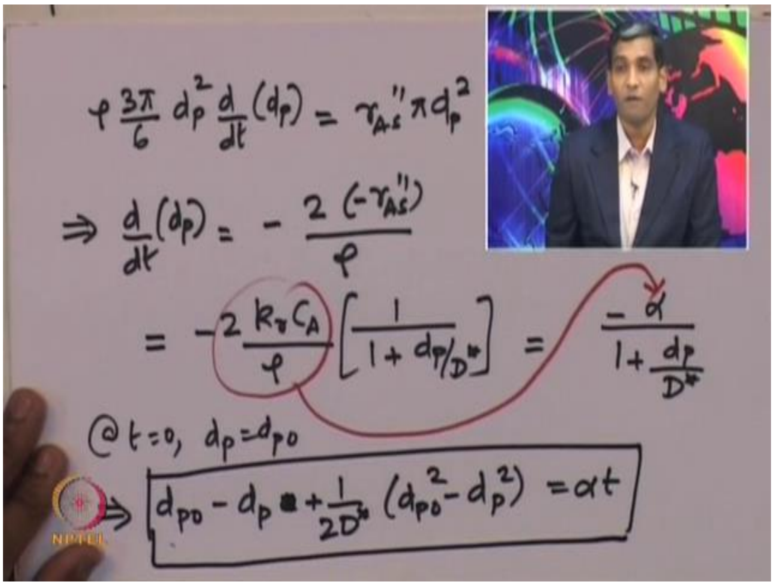

$$\rho \frac{3\pi}{6} d_p^2 \frac{d}{dt}(d_p) = r''_{As} \pi d_p^2$$

$$\Rightarrow \frac{d}{dt}(d_p) = - \frac{2(-r''_{As})}{\rho}$$

$$= -\frac{2 k_r C_A}{\rho}\left[\frac{1}{1+d_p/D^*}\right] = \frac{-\alpha}{1+\frac{d_p}{D^*}}$$

@ $t=0$, $d_p = d_{p0}$

$$\Rightarrow \boxed{d_{p0} - d_p + \frac{1}{2D^*}(d_{p0}^2 - d_p^2) = \alpha t}$$

So, now, this equation can further be simplified as row into 3 pi by 6 into d p square into that is equal to rAS into pi into dp square. So, this can be simplified as d by dt of dp that is the equal to minus 2 into minus rAS double prime divided by row. So, that is the expression for the rate of change of the diameter of the drug particle as a function of time and how it is rated as the surface reaction rate and the density of the particle. So, now this can actually be we know what is the rate; that can be minus 2 into kr into CA divided by row into 1 divided by 1 plus dp by D star.

This can be written as minus alpha divided by 1 plus dp by D star. So, that is the expression for rate of change diameter of the particles of the function of time. So, if you assume that this whole thing constant to alpha. So, we can rewrite this expression as d by dt of dp is equal to minus alpha by 1 plus dp by D star, where alpha captures the rate of the reaction divided by the density of the corresponding particles.

So, now, we can integrate this with the following initial conditions. At time t is equal to 0 initial size of the particles is dpo and based on this initial condition and the equation can be integrated. And integrated expression would be dpo minus dp plus 1 by D star 1 by 2 D star into dp square minus dp square that should be equal to alpha t. So, this provide relationship between the properties of the system and the diameter of the particle and time.

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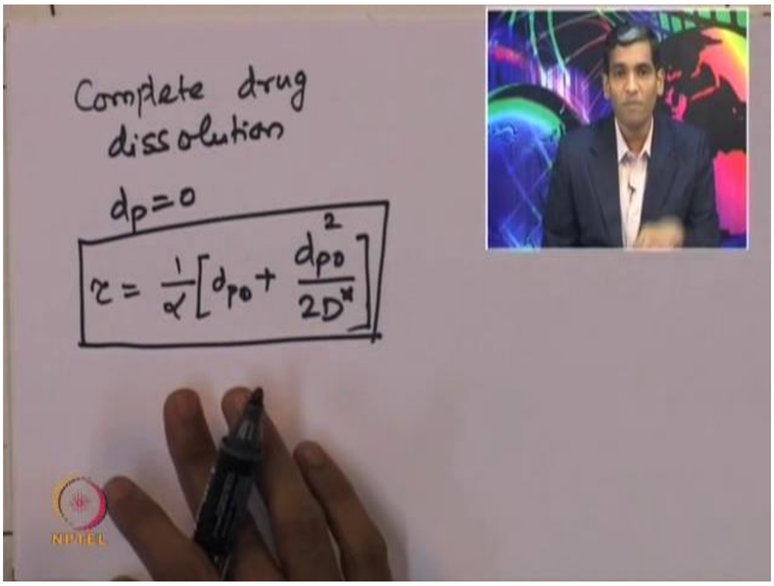

Complete drug dissolution

$d_p = 0$

$$\boxed{\tau = \frac{1}{\alpha}\left[d_{p0} + \frac{d_{p0}^2}{2D^*}\right]}$$

Now, in order to obtain a complete conversion for this problem for a obtain obtaining achieving complete conversion that is complete dissolution of the drug. So, the complete dissolution of the drug the dp should be equal to 0 that is all the particles are actually completely consume. So, and the time tow which is the taken for the complete conversion is given by 1 by alpha into dpo plus dpo by 2 D star square. So, that is the relationship between the time taken for complete conversion and the diameter of the particles and other properties of the system.

So, now, this is the expression this is for a mono dispersed particles,, but normally the drug which are actually administrator they are all poly dispersed particles are actually of different sizes. There is a population of particles and each of these particles can actually be a different sizes and all of them are actually simultaneously undergoing dissolution leading to the trinking of the particles. Now, only issue is that different particles will actually do different things because the size is different. Although, the reaction is same there dissolution rate are expected to be different because their sizes are completely different.

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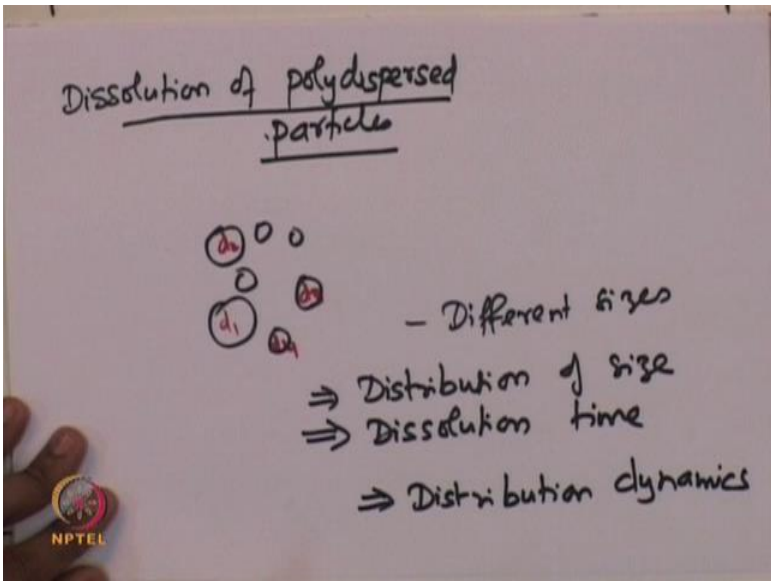

Dissolution of polydispersed particles

- Different sizes

⇒ Distribution of size

⇒ Dissolution time

⇒ Distribution dynamics

So, let us look at dissolution of let us see how to capture the dissolution behavior dissolution of poly dispersed particles. So, what is poly dispersed particles? Suppose, you have collections of particles which have different sizes for example, this big 1 could be size d1 and this could be d2 n d d3 and d4 and so on and so forth. There will be collection of particles each of these are different size. And so, there are particles of different sizes now not just that the initial stage that there particles will be of different size. There will be a distribution of sizes of particles although the time of dissolution has actually occurring.

So, therefore, there is a distribution there is a size distribution. And the question is to find out what is the dissolution time the objective to find the dissolution time. And in order to find the dissolution time for particles distribution 1 would 1 each is actually followed the distribution dynamics. The distribution dynamics have to be followed.

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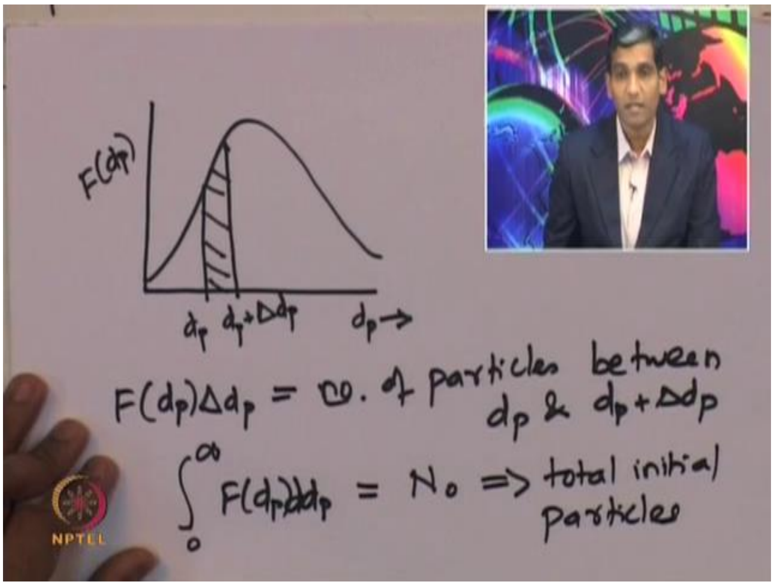

$F(d_p)\Delta d_p$ = no. of particles between d_p & $d_p+\Delta d_p$

$\int_0^\infty F(d_p)\Delta d_p = N_0 \Rightarrow$ total initial particles

So, let us look at what is distribution? So, suppose if I look at look at the plain of number of particles verses the fraction of the number of particles that are actually offer particular size. Then we that a except certain histogram where the location between say dp and dp plus delta dp which is a small increase in the particle small difference in the particle size.

So, in that case the area under the curve in this location is signifies the number of particles which are actually present in the system whose diameter between these 2 numbers. So, therefore, F dp multiplied by delta dp that is basically the number of particles between dp and dp plus delta dp. So, that is the number of particles and more over if we integrated this expressions from 0 to infinity F dp into dp to the differentiate of the diameter of the particle. That should be equal to n naught which is the total initial particles which are actually present.

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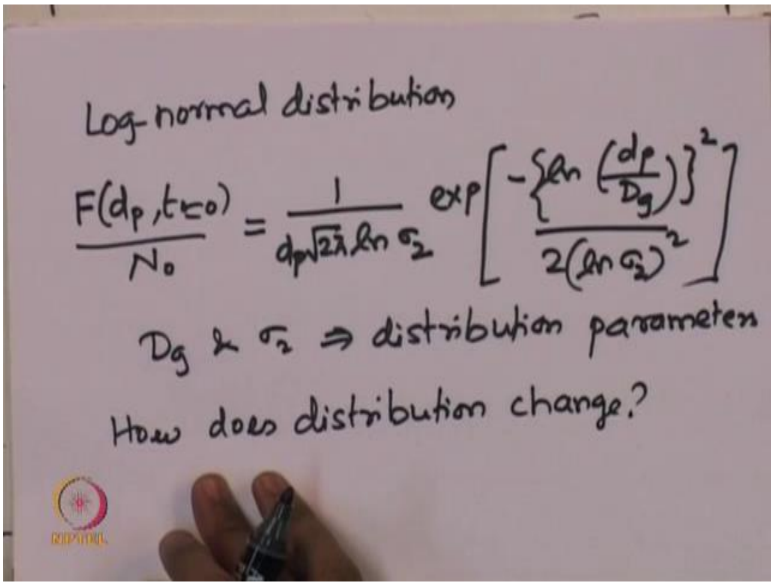

Log-normal distribution

$$\frac{F(d_p, t=0)}{N_0} = \frac{1}{d_p\sqrt{2\pi}\,\ln\sigma_2}\exp\left[-\frac{\left\{\ln\left(\frac{d_p}{D_g}\right)\right\}^2}{2(\ln\sigma_2)^2}\right]$$

D_g & $\sigma_2 \Rightarrow$ distribution parameters

How does distribution change?

If you assume that it follows a long normal distribution. Let us assume that the initial distribution of the particles they follow a log normal distribution. So, now the fraction of the fraction of particles whose size is dp and time t equal to 0 and that normalized by n not is actually given by 1 by dp square root of 2 pie of sigma 2 multiplied by of minus dp by Dg and square of divided by 2 time of sigma 2 square. So, that is the expression for the log normal distribution where Dg and sigma 2 are essentially the distribution parameters; these are the distribution parameters.

So, now the question is the in order to find out what is the dissolution time of the particles which are actually in this poly disperse system is to actually find out what is the how the distribution itself change. Instead of monitoring every drug particle it is better to monitor simply the population itself. So, the question is how does the distribution change? So, that is what we are going to look at.

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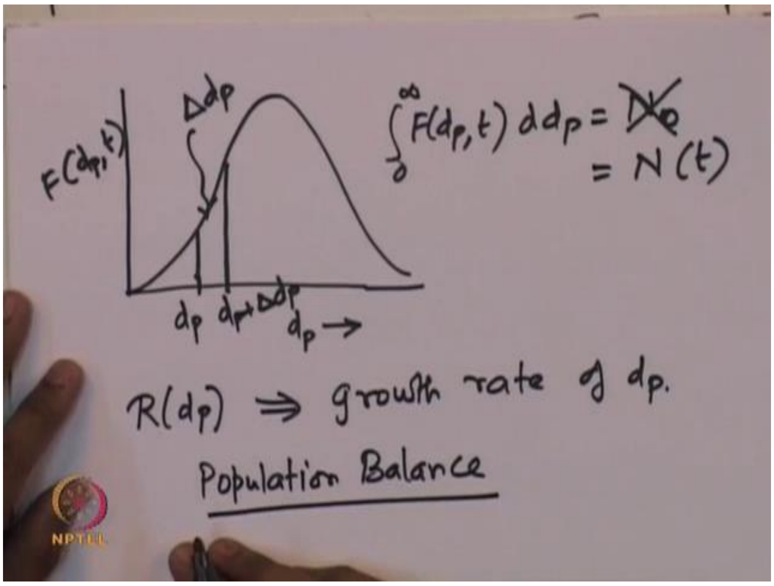

$$\int_0^\infty F(d_p,t)\, dd_p = \cancel{N_0} = N(t)$$

R(dp) ⇒ growth rate of dp.

Population Balance

Now, suppose if you look at the distribution at any time and if it is some general curve like this. Now, we can write a simple balance on the population of these drug particle suppose, if you take any small element between dp and dp plus delta dp. So, therefore, the thickness of this element delta d p if you assume the thickness of delta dp and by definition of the histograph, the integral of 0 to infinity F of d p come a t into dp should be equal to n not. That should be the the total number of particles that were actually initially present and because there are no new particles are added it only the particle actually dissolve and disappeared.

So, therefore, the integral under the curve after infinity if you assume that the particles are actually a have some size all types. Then that should be equal to the total number of particles itself. Now, if that is not the case then they should be a then should be a function of time. So, the number of particles will change because of these particles will and disappear and when that happens in this integral between 0 to infinity should actually be a function of time.

So, 1 other quantity which is required in order to the system is the growth rate suppose R dp is the growth rate of a every particle and of course,, it depends upon the size of the particles itself. So, that is the growth rate growth rate of particle whose diameter is dp then, 1 can actually write a population balance equation. In order to capture the dynamics of the whole distribution itself as the reaction actually proceeds.

So, the population equation balance can be written as the balance between the number of particles which are actually growing and reaching the diameter between dp and delta dp. And also we need to account for the particles which are already present in this small element dp and delta dp and they grow and the actually become bigger than a dp plus delta dp. So, which means that they leave the small element delta dp and there is no there is no addition of new particles because the once the drug is being fit it is just been dissolved. And. So, there is no other mechanism by which the particles are actually being added into that small element delta dp.

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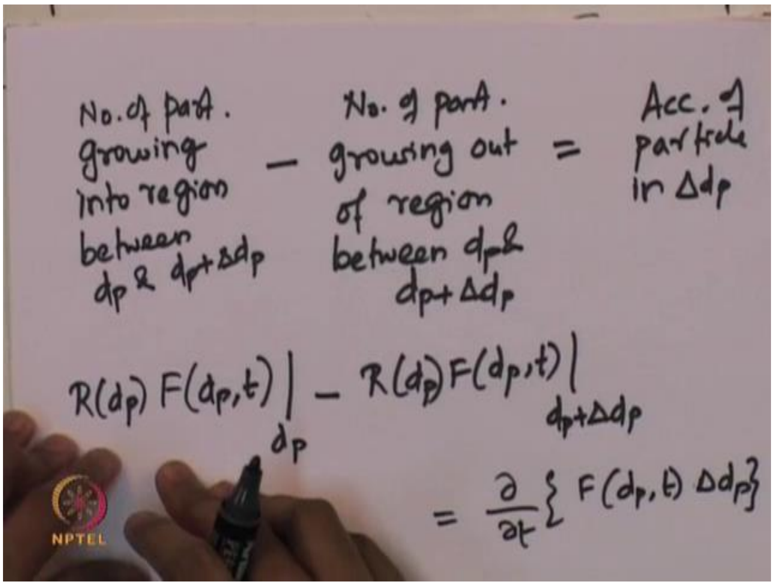

No. of part. growing into region between dp & dp+Δdp − No. of part. growing out of region between dp & dp+Δdp = Acc. of particle in Δdp

$$R(d_p)\,F(d_p,t)\Big|_{d_p} - R(d_p)\,F(d_p,t)\Big|_{d_p+\Delta d_p} = \frac{\partial}{\partial t}\left\{F(d_p,t)\,\Delta d_p\right\}$$

Then the other term you see the accumulation terms therefore, putting them altogether it be number of particle growing into region between dp and dp plus delta dp minus the of particles growing out of region between dp and dp plus delta dp. That should be equal to the accumulation of particles in delta dp in that small element. Now, suppose if R is the growth rate which is defined a short go.

Then the number of particles growing into the region between dp and dp plus delta dp is actually given by R into dp. So, that is the growth rate when the particle is right whose size is exactly dp and then that multiplied by the corresponding fraction. It will provide what is the number of particles that are actually going into the region in this small diameter. And that evaluated dp minus delta dp and that should be equal to d by dt.

So, that is the accumulation of particles and delta dp equal to F of dp, t multiplied by delta dp. So, that is the rate of change that is the rate of at which the particles are actually being accumulated in that small element.

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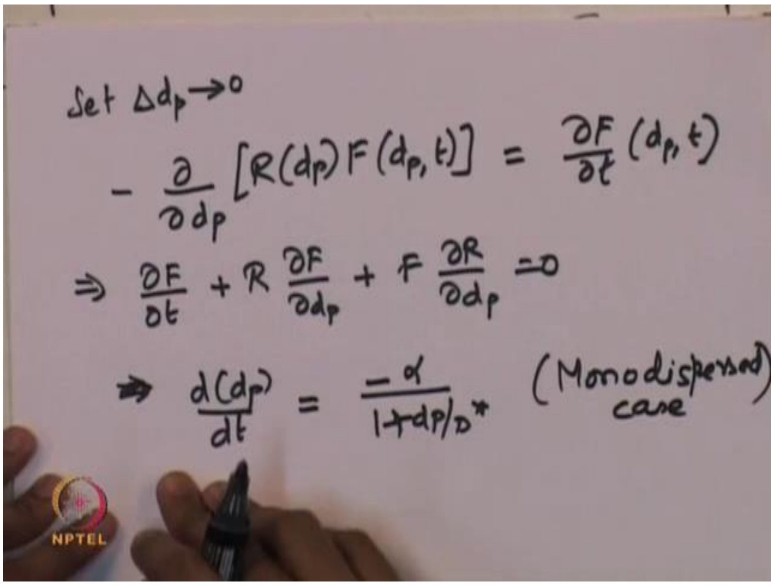

Set $\Delta d_p \rightarrow 0$

$$-\frac{\partial}{\partial d_p}\left[R(d_p)F(d_p,t)\right] = \frac{\partial F}{\partial t}(d_p,t)$$

$$\Rightarrow \frac{\partial F}{\partial t} + R\frac{\partial F}{\partial d_p} + F\frac{\partial R}{\partial d_p} = 0$$

$$\Rightarrow \frac{d(d_p)}{dt} = \frac{-\alpha}{1+d_p/D^*}$$

(Monodispersed case)

So, now rearranging this equation and setting delta d p equal to 0,. So, set delta dp equal to 0. Then can be written as minus by of dp of particle diameter f of dp, t that should be equal to F by t t. So, that is the expression for the population that is the population balance. So, now, what we do with this population balance? So, we can solve this equation in order to find the radius of the particles in order to find the how the distribution the radius distribution actually changes. So, now, this can actually be rewritten as dF by dt plus R into dF into d dp plus F into dR by d dp, that is equal to 0. So, now, where r d p is essentially the growth rate of the particle of size dp.

And if suppose in the earlier case, if the particle where mono dispersed we actually found out what is the growth rate. So, therefore, for every particle of a certain size that expression can be used as a growth rate of the particle of that particular size. So, therefore, from here it will be dp by dt that should be equal to minus alpha by 1 plus dp by D star. So, that is the rate at which the mono dispersed particles are actually are growing. So, that into the expression that into a population balance we will find that this is for the mono dispersed case.

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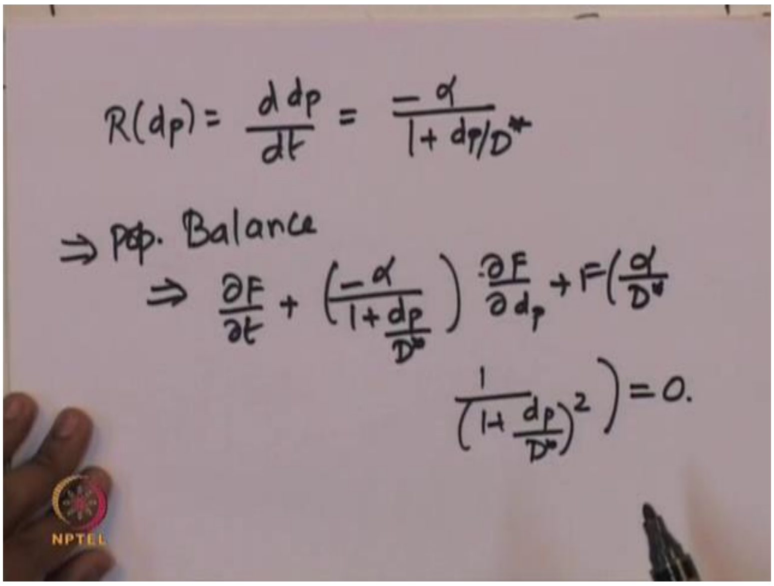

$$R(d_p) = \frac{d\,d_p}{dt} = \frac{-\alpha}{1 + d_p/D^*}$$

$\Rightarrow$ Pop. Balance

$$\Rightarrow \frac{\partial F}{\partial t} + \left(\frac{-\alpha}{1 + \frac{d_p}{D^*}}\right)\frac{\partial F}{\partial d_p} + F\left(\frac{\alpha}{D^*}\frac{1}{\left(1 + \frac{d_p}{D^*}\right)^2}\right) = 0.$$

So, plugging that into the expression we will find that the rate of R dp that is equal to d dp by dt that is equal to 1 plus d p by D star. And so, the population balance will be by dt plus minus alpha divided by 1 plus dp by D star into dF by dp plus f into alpha by D star 1 by 1 plus dp divided by D star whole square, that is equal to 0. That is the expression for that the population balance that actually captures how the dynamics of this distribution actually changes with time. How the how the distribution changes with time. So, now if we introduce, few dimension of quantity which actually useful in solving this problem.

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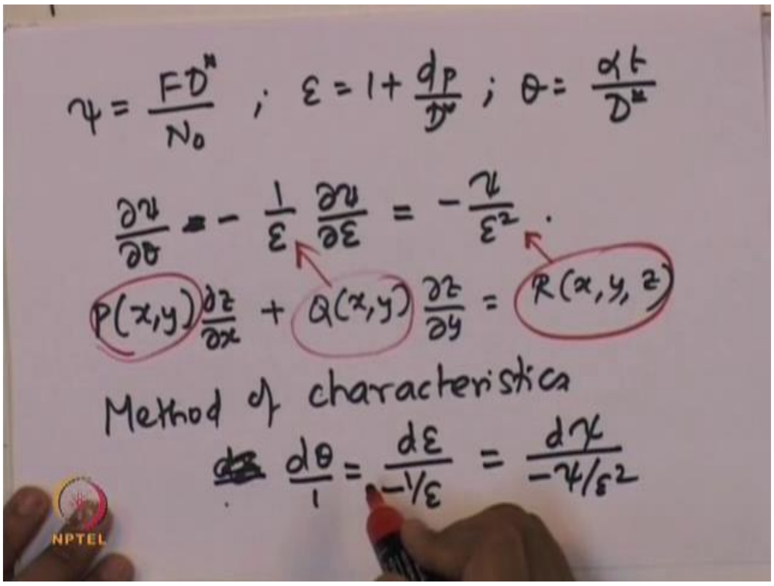

$$\psi = \frac{F D^*}{N_0} \; ; \; \varepsilon = 1 + \frac{d_p}{D^*} \; ; \; \theta = \frac{\alpha t}{D^*}$$

$$\frac{\partial \psi}{\partial \theta} = -\frac{1}{\varepsilon}\frac{\partial \psi}{\partial \varepsilon} = -\frac{\psi}{\varepsilon^2} .$$

$$P(x,y)\frac{\partial z}{\partial x} + Q(x,y)\frac{\partial z}{\partial y} = R(x,y,z)$$

Method of characteristics

$$\cancel{dx} \; \frac{d\theta}{1} = \frac{d\varepsilon}{-1/\varepsilon} = \frac{d\psi}{-\psi/\varepsilon^2}$$

So, equal to F d star divided by n not, where F is the distribution of the particles based on the size and D star is the ratio of the diameter when the mass transport rate and the reaction rate are equal to reach the and n not is the initial total number of particles. Then epsilon is defined as 1 plus d p by d star and theta is defined as alpha into t by d star. So, now, if you introduce these dimension less quantities we can rewrite the completion balance as, d psi by d theta that is equal minus 1 by epsilon into d psi by d epsilon minus that is equal to minus psi by epsilon square.

So, that is the expression. So, this equation actually very familiar differential equation form by which is also form p of x coma y into dz by dx plus q of x coma y into dz by dy that is equal to r of x, y,z. So, from here we can see that if P of x coma y is nothing,, but 1 and Q of x coma y is like 1 by epsilon and R of x coma y is like psi by minus epsilon square. So, the way to solve this equation is basically to use the method of characteristics is used the method of characteristics, where it is this problem is in the slightly different way.

So, dx by t d theta by 1 is equal to d epsilon by minus 1 by epsilon and that should be equal to d psi by minus psi by epsilon square. So, that is the way in which the a population balance equation which is actually written here can actually be post in terms of the method of characteristics.

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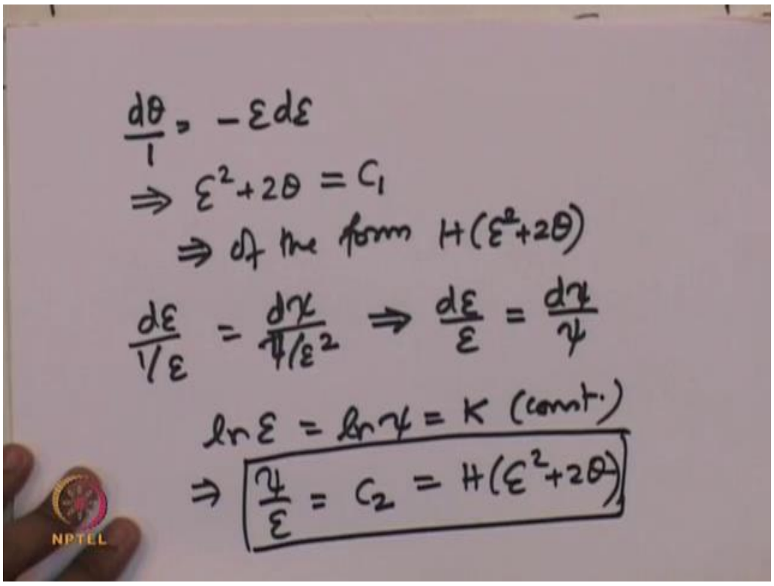

$$\frac{d\theta}{1} = -\varepsilon\, d\varepsilon$$

$$\Rightarrow \varepsilon^2 + 2\theta = C_1$$

$$\Rightarrow \text{of the form } H(\varepsilon^2+2\theta)$$

$$\frac{d\varepsilon}{1/\varepsilon} = \frac{d\psi}{\psi/\varepsilon^2} \Rightarrow \frac{d\varepsilon}{\varepsilon} = \frac{d\psi}{\psi}$$

$$\ln\varepsilon = \ln\psi = K \text{ (const.)}$$

$$\Rightarrow \boxed{\frac{\psi}{\varepsilon} = C_2 = H(\varepsilon^2+2\theta)}$$

So, now, the first 2 terms in the in the repost problem is basically it looks like d theta by 1 is equal to minus epsilon into d epsilon. So, from here we can find out that epsilon square plus 2 theta is equal to a constant C1 and that should be of the form of the form H of epsilon square plus 2 theta. So, that should be the functional form function depends on this particular expression and then next let us look at the other case, d epsilon by 1 epsilon that should be equal to d psi by psi by epsilon square.

So, this can be actually rewritten as d epsilon by epsilon is equal to d psi by psi which can be solved to obtain laun epsilon equal to laun psi that is equal to some constant k. That is a constant. So, from here we can find that psi by epsilon is nothing,, but some constant C2 and that can be equal to H of epsilon square plus 2 theta. So, that is the functional dependence. So, next we can actually see how to take this forward and find the distribution profiles.

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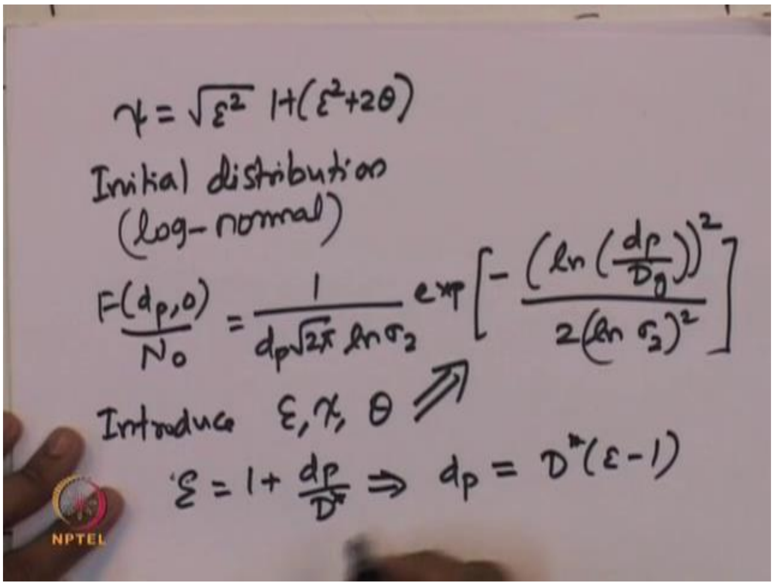

$$\psi = \sqrt{\varepsilon^2}\ H(\varepsilon^2+2\theta)$$

Initial distribution
(log-normal)

$$\frac{F(d_p,0)}{N_0} = \frac{1}{d_p\sqrt{2\pi}\,\ln\sigma_g}\exp\left[-\frac{\left(\ln\left(\frac{d_p}{D_g}\right)\right)^2}{2(\ln\sigma_g)^2}\right]$$

Introduce $\varepsilon, \psi, \theta$ $\Rightarrow$

$$\varepsilon = 1+\frac{d_p}{D^*} \Rightarrow d_p = D^*(\varepsilon-1)$$

So, suppose if we can rewrite the relationship between the psi and epsilon is equal to square root of epsilon square into H of epsilon square plus 2 theta. So, in order to obtain the final distribution, this is actually present in the definition of psi. So, psi is almost like non dimensional distribution of the various size of the particles which are of different sizes. So, if you look at the initial distribution initial distribution which is actually given by log normal distribution.

So, log normal distribution is as it goes here root 2 pi into laun sigma 2 into exponential of minus laun dp by D star dp by dg the whole square 2 divided by 2 laun sigma 2 square of 2. So, that is the initial distribution. No,w if you know the initial distribution, then we can actually introduce the transform variables. So, basically we introduce epsilon psi and theta into initial distribution and if you assume that, epsilon equal to 1 plus dp by D star.

So, this comes from the non dimensional form of epsilon. Then from here then we can get the d p is equal to d star into epsilon minus 1. Actually this is the non dimensional form of epsilon and from here we can find out the relationship between dp and the other parameters.

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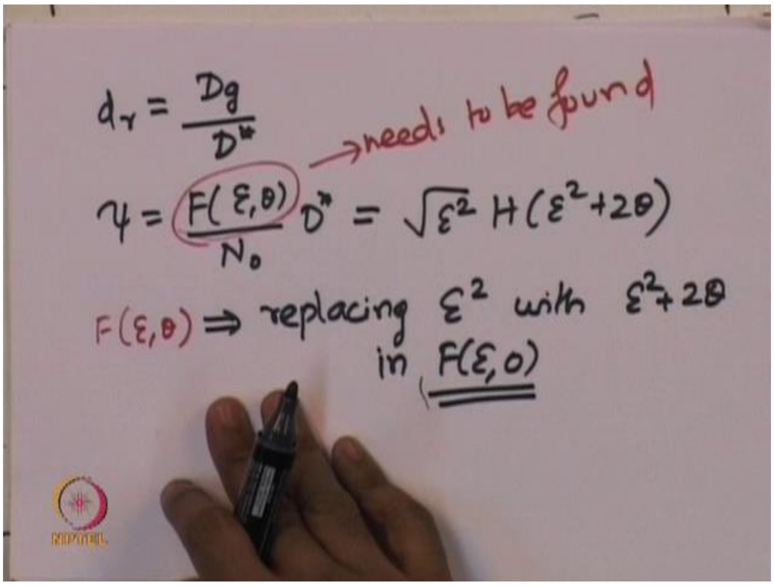

$d_r = \frac{D_g}{D^*}$

$\xrightarrow{}$ needs to be found

$\psi = \frac{F(\varepsilon,\theta)}{N_0} D^* = \sqrt{\varepsilon^2}\, H(\varepsilon^2+2\theta)$

$F(\varepsilon,\theta) \Rightarrow$ replacing ε^2 with $\varepsilon^2+2\theta$ in $F(\varepsilon,0)$

So, if you assume that dr if you assume a new variable d r is equal to Dg divided by D star where Dg is some parameter of the distribution and s star is the diameter at the mass transport rate and the reaction rate are equal. Then we can find out psi is equal to some f of epsilon coma theta divided by n not into d star that should be equal to square root of epsilon square into H of epsilon square plus 2 theta. So, that is the functional form of this variable psi.

So, now in if you want to find out what is the final distribution we need to find this expression epsilon coma theta. This expression need to be found in order to find out what is the distribution of the sizes. So, how can we do this it can be done by actually using the distribution at the initial the distribution at the initial state where the reaction has not started; then f of epsilon coma theta.

So, this can be obtained by simply replacing epsilon square with plus 2 theta in f of epsilon, 0. So, note that this is the initial distribution and final distribution can simply be obtained by replacing the epsilon square this initial distribution with epsilon square plus 2 theta. So, that serves as the solution methodology.

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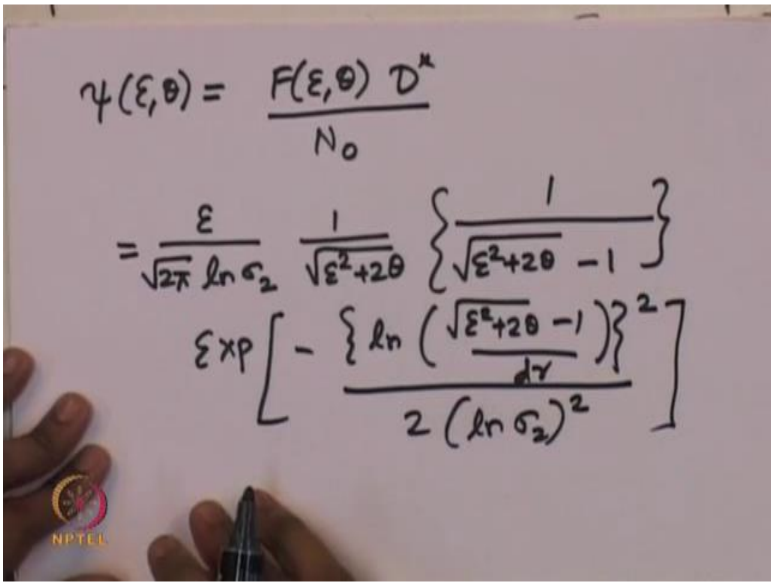

$$\psi(\varepsilon,\theta) = \frac{F(\varepsilon,\theta)\,D^*}{N_0}$$

$$= \frac{\varepsilon}{\sqrt{2\pi}\,\ln\sigma_2}\,\frac{1}{\sqrt{\varepsilon^2+2\theta}}\left\{\frac{1}{\sqrt{\varepsilon^2+2\theta}-1}\right\}$$

$$\mathcal{E}xp\left[-\frac{\left\{\ln\left(\frac{\sqrt{\varepsilon^2+2\theta}-1}{dr}\right)\right\}^2}{2\,(\ln\sigma_2)^2}\right]$$

So, now we can rewrite this as psi of epsilon, theta that is equal to f of epsilon coma theta. So, we can introduce we can now use the initial distribution in order to find out what is the value of psi. What is the expression for psi as the function of epsilon theta, and that would be equal to epsilon divided by square root of 2 pi into log sigma 2 into 1 by square root of epsilon square plus 2 theta into 1 by square root of epsilon square plus 2 theta minus 1 multiplied by exponential of minus laun of square root of epsilon square plus 2 theta minus 1 by d r and square of that divided by 2 into laun sigma 2 to the power of square 2. So, that is the distribution of any time in the non dimensional form. So, once we know this distribution we can look at the distribution as a function of time.

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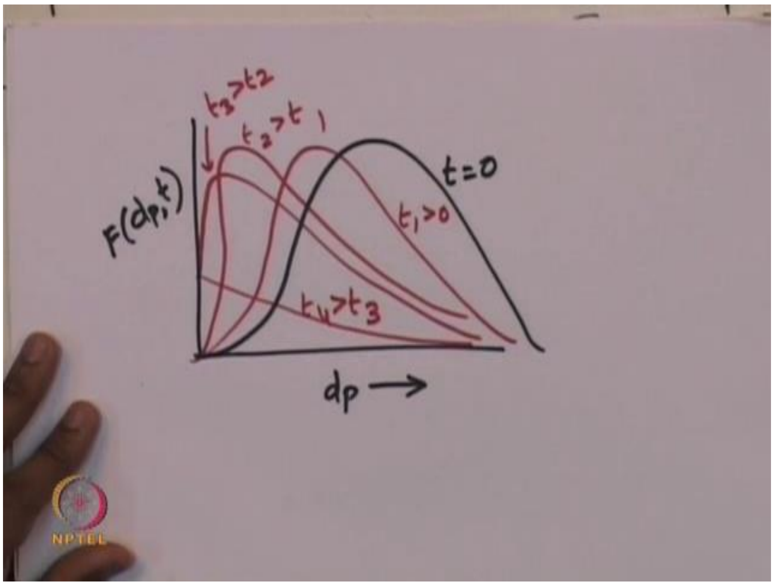

Suppose, this is dp particle diameter and this is F of dp come of time then suppose this is the initial distribution that is time t equal to 0, that is the initial distribution. Then as time progresses all the particles are actually undergoing the dissolution because of the hydrogen reaction.

So, time goes by distribution changes and this is t1 is greater than 0 and time further goes by more and more dissolution will happen and this will be t2 which will be greater than t1. Then further time will further time accesses then the distribution will be t3 which is greater than t2. And then eventually when conversion is going to be almost complete then distribution will look like this when t 4 which is greater than t 3. So, that is the kind of distribution that, 1 can actually obtain as function of time this poly dispersed particles which are undergoing dissolution.

So, let us summarize we have learnt in the last 3 lecture. We look at the fluid solid non catalytic hydrogen reaction and this can occur 2 more: one is where the particle size does not change and other one is the case where the particles size actually change as the reaction progress. And there are 3 different possible resistances which actually exist in this kind of a system: one of the gas film gas film resistance for diffusion resistance and the other 1 is ash layer diffusion resistance and the third one is the reaction controlling resistance offered because of the surface reaction.

So, these 3 under these 3 regime time that is taken for the unreacted time that is taken by the particles to reach a certain radius has been and calculated. And that for different geometries look into for both the shrinking or changing size particle case and constant size particle case. And then we look at the example of dissolution of mono dispersed particles and extended for a poly dispersed.

Thank you.