Lecture - 47
Fluid-Solid Non-Catalytic Reactions V

Friends it is a good time to summarize what we have learned in the last couple of lectures. So we are looking at the fluid-solid heterogeneously non-catalytic heterogeneous reactions and then we identified 2 possible cases 2 possible modes. One is the situation where the particle which is actually participating in the reaction it does not shrink with as the reaction progress and then in other situations where the particle which participates in the reaction actually shrink in size as the reaction progresses.

And then we looked at 2 possible models progressive conversion model and the shrinking core model and it was observed that the shrinking core model is more common in most of these situations and so we developed a model for the shrinking core model for both the particle size unchanging particle size and also for those particles which were shrinking in size.

And that for situations where if the overall reaction, overall conversion is actually controlled by a different rate controlling steps. For example, the diffusion of gas phase from the bulk through the gas film to the surface of the core or the diffusion of the species through the ash layer or it is the reaction controlling. So the expressions that we get for the time that is taken for the unreacted core to reach a certain size which is directly correlated with the conversion 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 for spherical particles so it can be summarized in this table here so for spherical particles suppose we take the constant size and varying or changing size these are 2 possible modes. Here changing size refers to the special case of no ash layer present. As noted in the earlier lecture the size can change even if the ash layer is present if the density of solid product and the reactants 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/tau where t is the time taken for the unreacted core to reach a certain radius because of the heterogeneous reaction that should be= the conversion of the solid itself which is directly related to the amount of solid that is reactant and then in changing size the expression for the same would be t/tau is 1-1-XB to the power 2/3.

Here tau is the time taken for the complete conversion that is all of the solids which is present is in the core has gone for complete reaction. Now next possibility is ash layer control ash layer diffusion control. So if ash layer diffusion is actually controlling the overall conversion in that case t/tau is given by 1-3*1-XB to the power of 2/3+ 2*1-XB so that is the expression for t/tau.

And of course in changing size the ash layer does not exist and therefore it does not offer any resistance to the overall conversion. This is the third case where the reaction is controlling the overall conversion, if the reaction control then t/tau is given by 1-1-XB to the power of 1/3 and here t/tau is given by 1-1-XB to the power of 1/3. In both cases the time taken for the unreacted core to reach a certain radius depends on the conversions 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 into the reaction control regime. Now all this we look for spherical particles what happens if it is other geometries for example if the (()) (05:06) of metals then normally it is not plated on a spherical particles it is plated on other kinds of geometries it could be a cylindrical geometry or it could be a flat plate geometry or it could be any other curvature.

Now let us look at 2 specific other geometries which are fairly common.

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One is the flat plate suppose if it is a flat plate and where the solid is now present in the flat plate and there is a fluid which is now coming on to the surface of the flat plate and the heterogeneous 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 case of constant particle size then for a flat plate one can actually define one can define conversion as 1-1/L where L is essentially the half thickness.

L is the half thickness of the plate that is actually being used as a solid reactant and if it is a film diffusion controlling if it is a film diffusion controlling regime in that case t/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 density of the particle * half thickness length scale/mass transport coefficient into concentration of species in the gas phase.

If it is ash layer diffusion control, then t/tau is essentially given by XB square where tau is

given by rho B L square/2 diffusivity into concentration of the species in the gas phase and if it is reaction controlled then t/tau is simply given by XB and tau is given by rho B L/k double prime which is the intrinsic rate constant multiplied by CAg intrinsic k double prime is the intrinsic specific rate and CAg is the corresponding gas phase concentration.

Now similar expressions have been obtained for cylinder geometry and they are as follows in this table.

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So for a cylindrical geometry the XB conversion of the solid is defined as 1-R/R0 (()) (08:00) is whole square. Now here R0 is the initial radius of the core R0 is the initial radius of the cylinder and R is the instantaneous radius of the cylinder. So with this definition if it is gas film diffusion control then t/tau is essentially given as XB and tau=rho B*R0 which is the initial radius/2 times kg into CAg.

So that is the time taken by the core for complete conversion and if it is ash layer diffusion control then t/tau is given by XB+1-XB multiplied by the natural logarithm of 1-XB where tau is the time for total conversion that is given by rho B*R0 square/4 De*CAg so that is the concentration of the species at the gas phase. And if it is reaction controlled then t/tau is essential given by 1-1-XB to the power of 1/2 tau=rho B* R0/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 are for basically constant size system and similar expressions can actually be worked out for varying size as well. We so far looked at the cases where the overall reaction is actually controlled by the resistance of 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 or if it is reaction control. So in reality this is not the situation in reality what happens is that all 3 resistances actually contribute.

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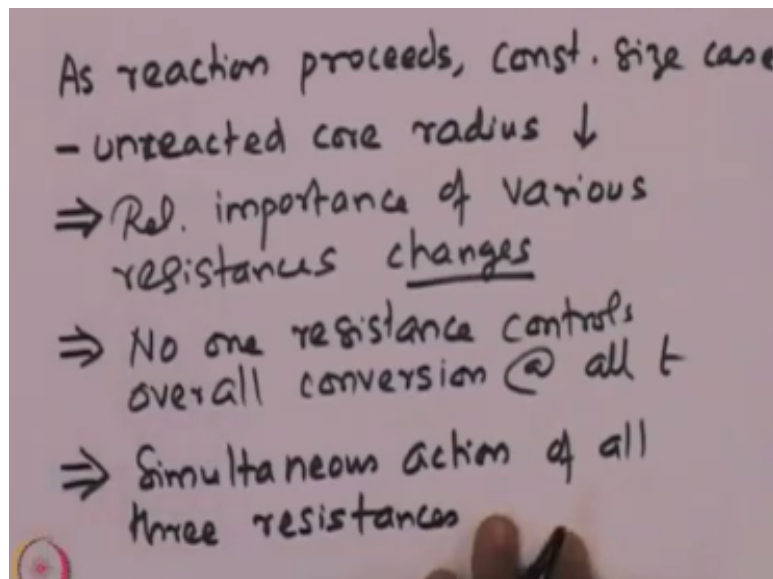
So as reaction proceeds and in fact that is true because as reaction proceeds even in the constant size case even the constant size case what is observed is that the of course the unreacted core radius is going to decrease unreacted core radius decreases as the reaction proceeds and therefore as a result the relative importance of various resistances is going to change.

So 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 one so no one resistance controls overall conversion all times all time t. So therefore it is important to 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 relates the rate of change of the radius of unreacted core with respect to time so all the other properties and concentrations of the system can actually be rewritten using a combination of all the resistances.

And the rewritten model will be dR/dT that will be= -CAg/rho B CAg is the gas phase concentration rho B is the density of the solid that is used/R square/R0 square*kg+R0-R/ diffusivity *R/R0+1/k double prime that is the specific reaction rate. Now here it is assumed that the volume fraction of the solid in the unreacted core is approximately=1 and so there are 3 terms here which corresponds to 3 different resistances. So the first one here this corresponds to the gas film resistance.

And this corresponds the ash layer this corresponds the diffusion in ash layer and the last term corresponds the reaction resistance. Resistance due to the heterogeneous reaction that is occurring on the surface of the unreacted core. Now suppose this is for a constant size system so if the particle size does not change this is for the constant size system. Suppose the same thing can be written 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 resistance due to the ash layer which is present in this expression here. So for shrinking particles there is no ash layer so therefore we can write this expression as dR/dt is –Cag/rhoB/1/kg+ 1/k double prime where k double prime is the specific rate and kg 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 a certain type which is ongoing such kind of a fluid-solid non-catalytic heterogeneous 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 when they go into the body they have to dissolve and it is important to understand how much time does it take for the drug which is a solid particle to dissolve and that the dosage of the drug actually strongly depends on the time taken for complete dissolution.

So therefore it is important to model this from the pharmacokinetics stand point of view. So let us look at this problem.

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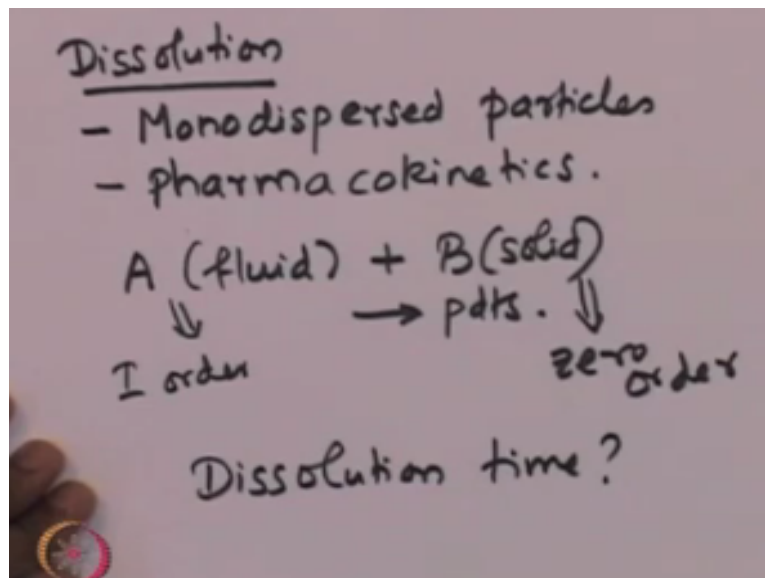
So dissolution of solid particles suppose if we assume that there are all these drugs which are given inside they are all monodispersed particles that is all the particles that are actually in the drug are of same size. This is not true always, but let us assume to start with that all particles are actually same size that is it is a monodispersed system. And then 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 species A which is basically in the fluid stream that reacts with certain solid which is essentially the drug particle and that leads to formation of products. Now if we assume that the fluid A actually reacts with the core which contains the solid material and if we assume that it is first order with respect to the fluid the reaction rate is first

order with respect to fluid and zero order with respect to the solid which is present.

Then the question is what is the dissolution time? So we need to estimate the objective of the problem is to find the dissolution time the time that is taken for dissolution of these particles.
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So now we can observe we can actually observe that the rate of mass transport the rate of mass transfer to the surface is actually equal to the rate of surface reaction. Why is this because the particles are expected the property of the drug are always such that the particles are expected to dissolve and so the particle this is actually a 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 transfer to the surface should be equal to the rate at which it is being consumed for the surface reaction. So therefore we can write there are WAr if that is the flux at which the species is actually travelling from the bulk gas phase to the surface of the solid that is equal to kg* CA-CAS where CA is the bulk concentration and CAS is the surface concentration.

And that should be=the reaction rate rA double prime and that is= if kr is the specific reaction constant multiplied by CAS so that is the surface concentration and this is the net reaction rate. So this is the reaction rate and this is the mass transport which corresponds to the mass transport. So from here we can actually eliminate CAS so note that CAS is a quantity which cannot be actually measured experimentally, but CA is the bulk concentration.

And that can actually be a measured. So we need to eliminate CAS which is not a measurable quantity so kg*CA divided by kg+kr. So plugging in this back into the expression for WAr we find that double prime that is=kr*kg CA/kr that is=CA/1/kg+1/kr. So therefore if we know the mass transport coefficient and the specific reaction rate then we will be able to actually calculate the required quantities such as the dissolution time.

So therefore now there is a need to find out what is this mass transport correlation so we can use correlation in order to find the mass transport coefficient kg.

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So suppose if we assume that the particles are small so under small dp and if there is no shear stress at the so there is no shear stress at the boundary of the fluid and the solid then we can actually using the Froessling correlation we can find out that Sherwood number which is= mass transport coefficient into diameter of the particle/corresponding (()) (21:29) that is approximately=2.

So from here we can find out that the mass transport coefficient is given by 2 times diffusivity/the corresponding particle diameter of the particle which is actually being dissolved. So plugging into the back into the expression for (()) (21:48) we find that WAr=kr*CA 1+kr/kg and that=kr*CA/1+kr* dp/ 2 times De and with this can be rewritten as kr*CA/1+dp/D star.

So D star is nothing, but the ratio of 2 times De*kr so that is what this D star. So D star the meaning of D star is that it basically tells you the diameter at which the mass transport and

the reaction rates are actually equal. So if we look at what is the expression for D star.

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

$$d_p > D^* \Rightarrow \text{M.T Controlling}$$

$$d_p < D^* \Rightarrow \text{Rxn Controlling}$$

D star is 2 times De/kr and that is essentially the diameter at which the mass transport rate and the reaction rate are equal. So therefore if the diameter of the particles if this is larger than D star then it can be expected that it is mass transport controlling. While if the particle diameter is <D star then it is actually expected to be a reaction controlling scheme the overall conversion is expected to be reaction controlling.

So now in order to find the radius of the particle as a function of time we can now write a mole balance on the solid particle.

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Mole balance on solid particle

$$\text{In} - \text{Out} + \text{Gen} = \text{Acc}$$

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

Equimolar counter diffusion

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

And the mole balance goes as here. Mole balance on solid particles so whatever rate at which

things are coming inside-whatever rate at which the particles are leaving out+ generation should be=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 is actually being reacted so that is a (()) (24:19) the generation term. So if rBs is the rate at which the solid is being consumed at the surface of the particles multiplied by pi*dp square that is the surface area of the solid particle and that should be=d/dt * density*volume of the spherical particles. So suppose if we assume equimolar counter diffusion then the –rAs double prime that is the rate at which the species A is actually consumed because of the heterogeneous reaction.

That should be=-rBs the rate at which the solid is being consumed this is because of the equimolar counter diffusion and the stoichiometry which is associated with the particular reaction.

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So this equation can further be simplified as rho*3 pi/6*dp square * that is= rAs * pi*dp square. So this can be simplified as d/dt of dp that is=-2-rAs double prime divided by rho so that is the expression for the rate of change of the diameter of the drug particle as a function of time and how is it related to the surface reaction rate and the density of the particle. So now this can be actually be we know what is the rate so that can be rewritten as -2*kr*CA/ rho* 1/1+dp/D star.

And this can rewritten as –alpha/1+dp/D star. So that is the expression for rate of change of the diameter of particle as a function of time. So if we assume that this whole thing is a constant like alpha so we can rewrite this expression as d/dt of dt=-alpha/1+dp/d star where alpha captures the rate of reaction/by the density of the corresponding particle. So now we can integrate this with the following initial condition at time t=0.

So initial size of the particle was dpo and based on this initial condition in the equation can be integrated expression would be dpo-dp+1/D star ½ D star *dpo square-dp square that should be=alpha t. So this provides the relationship between the properties of the system and the diameter of the particle and time. Now in order to obtain a complete conversion for this problem for obtaining, achieving complete conversion that is for complete dissolution of the drug.

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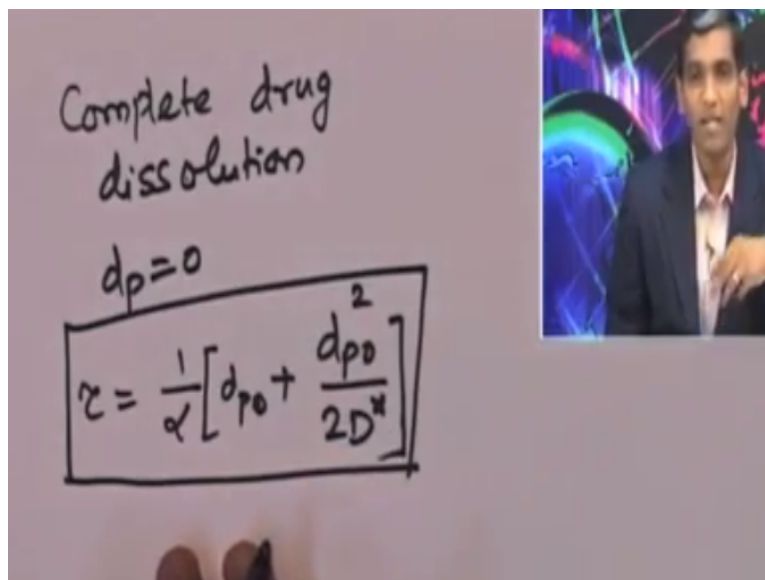
So for complete dissolution of the drug the dp should be=0 that is all the particles are actually completely consumed and so at the time tau which is the time taken for complete conversion is given by 1/apha*dpo+ dpo/2 D star square. So that is the relationship between the time taken for complete conversion and the diameter of the particle in other properties of the system.

Now this is for monodispersed particles, but normally the drugs which are actually administered they are all polydispersed that is particles are actually of different sizes. There is a population of particles and each of these particles can actually be of different sizes and all of them are actually simultaneously undergoing dissolution leading to the shrinking of the

particle.

Now the only issue here is that different particles will actually do different things because the size is different. Although the reaction is same their dissolution rates are expected to be different because their sizes are completely different.