Chemical Reaction Engineering

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Lecture No. # 26

Problem solving : Heterogeneous reactions

Friends, in last few sessions we have been looking at heterogeneous reactions or in other words, we have reactions which do not occur in a single phase, but more than one phase is involved. Now when you have more than one phase involved in a reaction, there are interfaces that is, the boundaries between these two phases.

As soon as, we have boundaries at the interface or boundary between these two phases, there is a transfer limitation which comes into picture that is how fast or how slow, the material gets transferred from one phase to another phase and thus we bring in the transport phenomena into the domain of chemical reaction engineering and we have spent quite a bit of time discussing about the kinetics of such processes.

And in this session we will look at few examples or we will try to solve few examples which relate to these heterogeneous reactions. But, before we do that let us quickly summarize as to what we have seen in this third module of this course namely on heterogeneous reactions.

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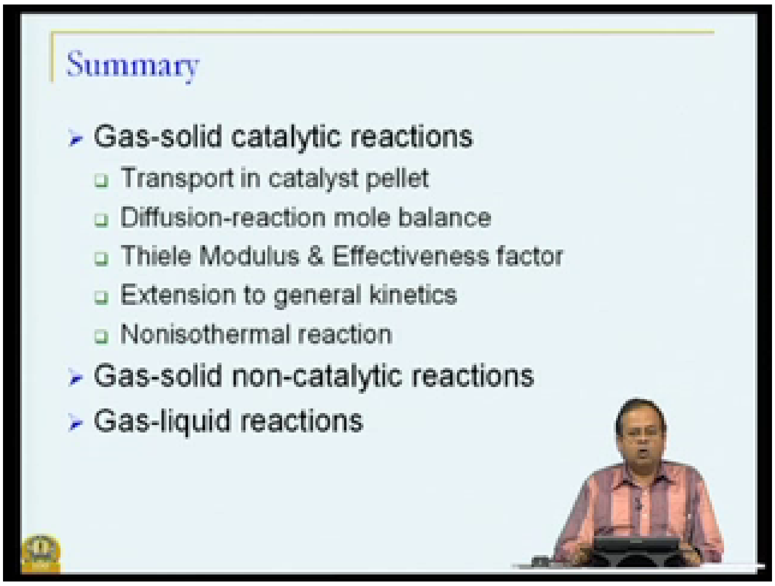

Summary

- Gas-solid catalytic reactions
  - Transport in catalyst pellet
  - Diffusion-reaction mole balance
  - Thiele Modulus & Effectiveness factor
  - Extension to general kinetics
  - Nonisothermal reaction
- Gas-solid non-catalytic reactions
- Gas-liquid reactions

So, we started with gas-solid catalytic reactions and discussed extensively on these reactions. So, we talked about for example, the transport in the catalyst pellet. Firstly, we identify now that there are several steps, before reaction can take place and these are transfer of reactants from the bulk to the surface of the catalyst, then from the surface of the catalyst to inside the catalyst, then adsorption of the reacting species on to the surface chemical transformation of these active adsorbed species into a product, still adsorbed unto the catalyst surface.

Then, desorption of the product from the catalyst surface it is travel backwards from interior of the catalyst to the surface of the catalyst and from surface of the catalyst eventually into the bulk of the catalyst.

So, we have two steps which involve external mass transfer that is, bulk to the surface, two steps which involve internal mass transfer namely transport within the catalyst pellet and three steps which typically characterize the chemical reaction that is, taking place by interaction of our reactants and products with the active surface.

So, this transport process will now also play a crucial role in determining the kinetics of the reaction. Now, how does this transport process occur? We have bulk diffusion in the or diffusion rather in the bulk phases, but when it comes to the catalyst pores which can be of micron sizes or even smaller, there are other factors such as Knudsen diffusion, viscous flow come that is capillary flow also come into the picture.

So, while we can characterize the bulk flow by the diffusion coefficient, we have to worry about the diffusion coefficient of the Knudsen regime and the capillary flow and so on. And we have tried to put all this together into what we call effective diffusivity of a reactant in the catalyst.

The catalyst effective diffusivity is influenced by several factors one of them is of course, there is multi component diffusion. That is there is no not just binary diffusion species a diffusing in b, but we have a diffusing in a mixture of b c d and so on and in turn b diffusing in mixture of a c d and so on. So, that is one modification that comes in.

The second modification, as I said it is a Knudsen diffusion that is if the mean free path of the gas molecule is large then, there is a possibility that diffusion occurs not because of molecule to molecule interaction, but because of molecule to wall of the catalyst pellet interaction and this is referred to as Knudsen diffusion. When can these happen mean free paths is inversely proportional to the pressure. So, under those conditions we will have Knudsen diffusion playing an important role.

The third thing is the capillary flow that is, this is equivalent to saying there is a flow a through a capillary of micron size and there is therefore, a pressure drop between the inlet of the pore and the exit of the pore and this pressure drop drives the viscous flow or the convective flow and therefore, we have viscous flow influencing the overall diffusion process.

Apart from this, we also have to worry about two things that we discussed. What are those, number one is the fact that when we try to describe this diffusion or diffusion process, we are essentially looking at from the bulk perspective. So, what is the diffusion of reactant? Let us say a into the catalyst and this we normally define per unit catalyst area, but we realized that out catalyst is not an void catalyst that is, the entire area or cross section if you look at the entire area is not available for flow.

What is available for flow is only what are the void volume or void fraction absolvent void a volume or the fraction to total volume we call void fraction. So, the diffusivity gets reduced by this factor absolvent that is one aspect. The second aspect is that we always talk about diffusion in the direction of the bulk flow.

Now, inside the catalyst the path that these molecules travel is not the same or not in alignment with the bulk flow of the reactant and product molecules or in other words the path it follows is much more tortuous, because these pores are not parallel pores from one end of the catalyst pellet to other end. They can be of any paths with lot of twist and turns and so on or in other words it is a tortuous path. So, the diffusion coefficients get further reduced by the factor what we call tortuosity. So, we divide it by the tortuosity factor and this is what determines the effective diffusivity.

We then wrote diffusion reaction mole balances for these reacting the species. Now moment we say that we have diffusion and reaction two different processes and within diffusion there is internal diffusion and external diffusion with each of these process having it is own characteristic rate or time scales. Time scales are roughly one can in a loose term say inversely related to the rate. If the rate is large time, scales are small; if rate is small, time scales are large.

So, we now would like to know given this process of diffusion and reaction, how do we characterize, which are the slow processes, which are the fast processes and so on and for that we defined what we call the Thiele modulus which rates the time scales for diffusion to time scales for reaction. So, if diffusion time scales are very large compared to reactions time scales, the Thiele modulus is has a large value which implies that we are in a diffusion controlled regime.

On the other hand, if the reaction time scales are very large we are in the kinetic regime. So, this is how we characterize or rate these two processes and along with this we also rate the reaction rate that we observe. Now, what is this rating? See, we have diffusion and we have reaction and together determine what rate we will observe. So, we can consider a scenario, where there was no diffusion and then do a rating of the observed rate to what would have been the rate, if diffusion was not there and this rating parameter we call it as effectiveness factor.

We saw how these effectiveness factor and Thiele modulus are related to each other. For example, when Thiele modulus is very small, effectiveness factor is for most of the reactions close to unity or rather why most of the reactions all the reactions are close to unity. On the other hand if the diffusion is very slow; that means, Thiele modulus is very large, the effectiveness factor varies inversely as Thiele modulus.

We initially had this discussion based on isothermal, first order irreversible reaction in a catalyst pellet, but then one by one go on extending this concept to a general kinetics to non isothermal reactions to different geometries of the reactions and saw there is some kind of uniqueness in relationship between effectiveness factor and Thiele modulus.

What does this Thiele modulus depend on? It depends on the operating conditions such as concentrations partial pressure for a general kinetics, it depends on the rate constant of the reaction, it depends on the diffusion coefficient. Then we went on to look at gas-solid non-catalytic reactions. These gas-solid non-catalytic reaction share several features of gas-solid catalytic reactions namely the transport aspect is more or less similar.

The major difference between the catalytic and non-catalytic reactions is that the solid what we are looking at in a non-catalytic reaction is not a static material, but it is dynamic. That is it is size for example, changes with time and therefore, making gas-solid non-catalytic reactions in time dependent processes whereas, catalytic reactions we could easily assume quasi steady state, as far as the diffusion process is concerned and look at the steady state analysis.

What happens, because of this time dependent characteristic? We actually now have to define how do we calculate the conversion or what is the time for entire catalyst or entire reaction to be over and this one way of doing this is to find out for example, if you are looking at case where solid is disappearing, what is the time required for complete disappearance of the solid such as burning of carbon for example.

In which case our hundred percent conversion refers to radius of the carbon particle going to zero and then we calculate the time required and based on this time required this will depend upon the factors whether diffusion is limiting, reaction is limiting and so on.

We also talked about gas-liquid reactions, once again diffusion becomes or transport phenomena becomes important, but here we focused more on what happens to the reaction as the kinetics of the reaction changes for example, when here is a very slow reaction.

So, first of all here we assume that the reaction occurs, because of transfer of material from the bulk gas phase to the interface, then transfer from the interface on the gas side to interface on the liquid side and one way common way of dealing with this is to assume

Henry’s law some equilibrium relationship between gas concentration and or gas partial pressure and concentration in the liquid. Then reaction then transfer from interface in the liquid to the bulk liquid and then the bulk liquid reaction.

So, now depending upon the variation in the rate of the reaction, we came across various scenarios. For example, if rate is very slow to the extent that we can neglect reaction in the interface or boundary on the liquid side that is one scenario. As the reaction rates increase this boundary also starts playing a crucial role.

So, some reaction can take place in the boundary as well to the other extreme, where reaction is almost instantaneous very fast, and then the reaction is reduced to actually a plane in which there is a contact between gas and liquid plane located between the thin boundaries on the liquid side.

Here in gas-liquid reaction one also can talk about rating these diffusion processes and looking at reaction that we observe with reaction that would have been there, if the diffusion process was not limiting. But, more convenient and practical way of looking at gas-liquid reactions is looking at the enhancement factors, because what essentially and this idea comes from the fact that in absence of reaction there still can be mass transfer and which would be simple absorption process depending on the saturation concentration of the gas in the liquid.

So, we would have got this rate without any reaction rate of absorption. Now if you look at gas-liquid reaction even when the reaction is taking place, we can also still look at the rate of absorption. Our observed rate is nothing, but the rate at which gas is disappearing from the gas phase gaseous reactant.

So, we can still look at it, but now rate this with what would have been the rate of these disappearance, if reaction was not there and this rating parameter, we call it as enhancement factor and now it turns out that because there is a reaction we could have enhancement factors which by as it is name suggests has magnitudes far greater than one. In fact, you design your liquid system in a way that enhancement factors are as large as possible.

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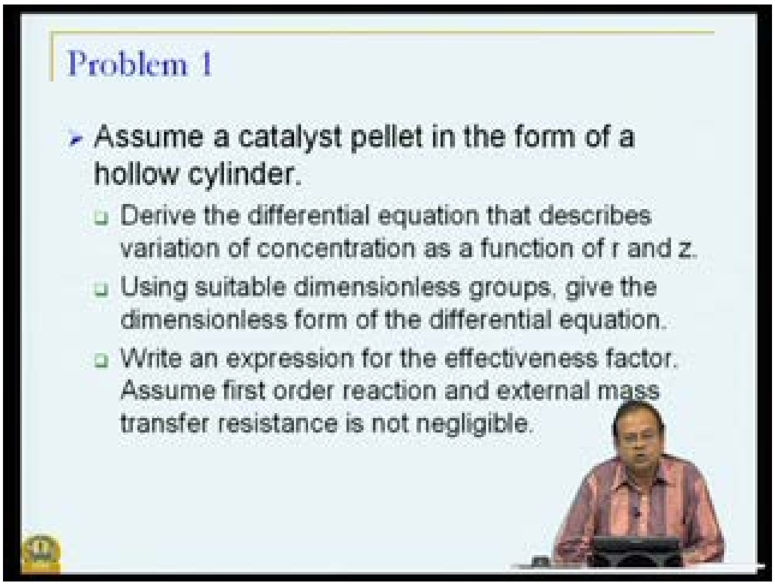

Problem 1

- Assume a catalyst pellet in the form of a hollow cylinder.
  - Derive the differential equation that describes variation of concentration as a function of r and z.
  - Using suitable dimensionless groups, give the dimensionless form of the differential equation.
  - Write an expression for the effectiveness factor. Assume first order reaction and external mass transfer resistance is not negligible.

So, this is how what we basically discussed in our previous modules. So, now let us turn our attention to few problems in this domain. The first problem says that, we considered geometries which were spherical cylindrical and so on or flat geometry. But, let us say that it is in the form of a hollow cylinder and we are supposed to derive the differential equations that describe the variation of concentration not only as a function of radius, but also as a function of axial distance.

Using suitable dimensionless groups give the dimensionless form of this differential equation and then ultimately define a suitable expression for effectiveness factor. Assume that it is a first order reaction, because we want to keep our discussion simple.

But, we have seen enough cases to suggest that whatever, is applicable for first order reaction with little bit of variation major ideas being same is applicable for general reactions as well and mass transfer external mass transfer is also negligible. So, let us try to write this mass balance equation.

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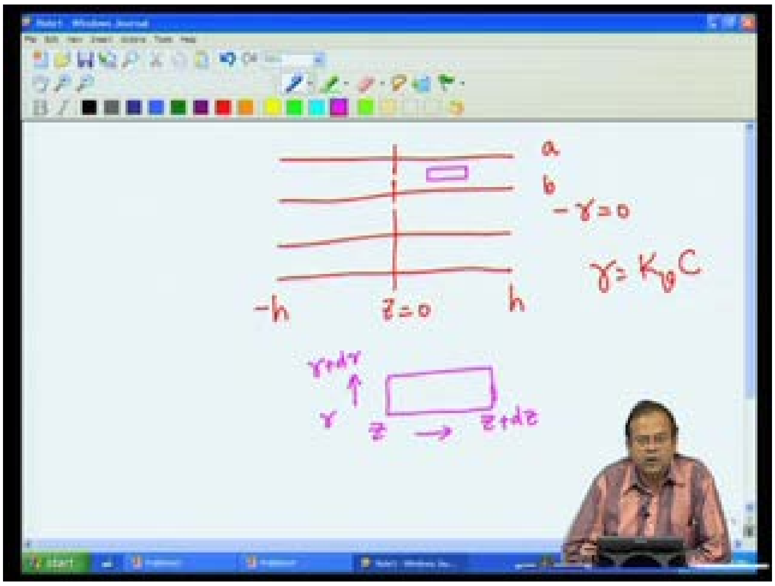

So, what is first of all let us start with our geometry. So, we have a cylinder, but it is hollow. So, let us put the centre point of this as z equal to 0 and let us say half width half length is h. So, we have z going from minus h to h and again let us put the centre axis r equal to 0 here and the radius going from a to b.

Let us reverse the order ,it does not make much difference. So, we are getting going from a to b. Our rate of our reaction is first order, c is the concentration of my reactant, it is a first order reaction, this two r s are different this is the radial position and this is the rate of the reaction. So, we keep that in mind.

So, we want to now write a mass balance. So, what we will do is we will consider a small cross section in the cylinder not in the hollow part, but in the part where the catalyst material is there and write a mass balance. How do we characterize this small element? The same way as we normally do us say that this is z and z plus d z along the axial direction and this is r and r plus d r along the radial direction.

So, the idea here is that we have variation of concentration both along the radial direction as well as axial direction.

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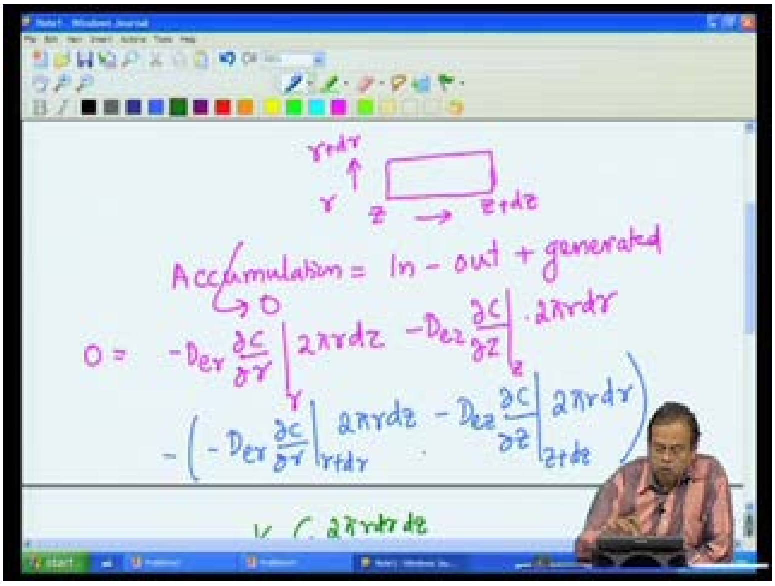

Accumulation = In − out + generated

Accumulation → 0

$$0 = -D_{er}\frac{\partial c}{\partial r}\Big|_r 2\pi r dz - D_{ez}\frac{\partial c}{\partial z}\Big|_z \cdot 2\pi r dr$$

$$-\left(-D_{er}\frac{\partial c}{\partial r}\Big|_{r+dr} 2\pi r dz - D_{ez}\frac{\partial c}{\partial z}\Big|_{z+dz} 2\pi r dr\right)$$

$$k\ C\ 2\pi r dr\ dz$$

Our mass balance is a mass balance, it is same irrespective of whether, it is a hollow cylinder, it is a reactor or whatever is there and that is namely accumulation equal to mass, that is coming in minus mass that is going out plus mass or moles we talk in terms of mass. So, understood that we are talking in molar concentrations and molar mass basis. So, this is my mass that is coming in going out we are interested in a steady state balance. So, this is 0, now let us try to find out what is coming in.

Now, coming in is both from radial direction and also from axial direction. So, let us talk about radial direction, if my flux is minus D e r dou c by dou r. I am now writing a small subscript r to say that diffusivity in the radial direction, which could be different from diffusivity in the axial direction, but that is a detail, but let us call it as minus D e r at r. So, this is flux. So, has to be multiplied by the appropriate area and what is that area, this length is d z.

So, that area is the surface area d z this is what is coming in at r; what about z, same thing at given cross section. So, this is what is coming in multiplied by the area and what is the area, if you look at the z direction 2 pi r d r. So, this is what is coming in.

Now, what is going out at r plus d r and at z plus d z. What is going out will be a similar term. So, minus because in minus out, minus D e r dou c by dou r at r plus d r area 2 pi r d z. So, that is going out in a radial direction at r plus d r. What is it that is going out in the axial direction into 2 pi r d r.

So, that is what is going out and what is being generated, what is being generated is actually this is getting converted. So, that is minus k v into c and what is the area for this the area for this will be 2 pi r d r d z, rather the volume, because the rate is per unit volume and the volume of this small cross sectional element is 2 pi r d r d z.

So, this is my general mass balance equations. So, let us repeat once again, we have a hollow cylinder going from minus h to plus h as it is length and radius from which is the outer radius to b which is the radius of the inner part and from 0 to b is a hollow portion. In this to write a mass balance, we selected a small cross section between z and z plus d z and r and r plus d r. So, this particular small portion and wrote a mass balance for what is coming in, what is going out plus, what is getting generated.

In writing in and out the idea is flux times the area and for generated, it is rate times the volume, because the rate is defined in terms of per unit volume. So, that all units all terms I have same dimensions namely mass.

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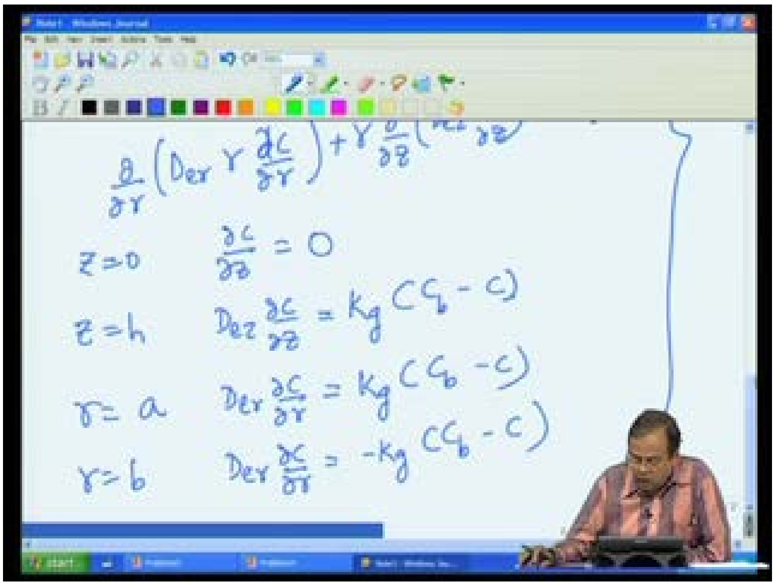

$$\frac{\partial}{\partial r}\left(D_{er}\, r\, \frac{\partial c}{\partial r}\right) + r\frac{\partial}{\partial z}\left(D_{ez}\frac{\partial c}{\partial z}\right.$$

$z = 0 \qquad \frac{\partial c}{\partial z} = 0$

$z = h \qquad D_{ez}\frac{\partial c}{\partial z} = k_g(C_b - c)$

$r = a \qquad D_{er}\frac{\partial c}{\partial r} = k_g(C_b - c)$

$r = b \qquad D_{er}\frac{\partial c}{\partial r} = -k_g(C_b - c)$

So, now to this expression, we can divide the entire expression by 2 pi r d r d z and as we do in deriving any equation take limit as d r goes to 0, d z goes to 0 and if we do that these mass balance equation will reduce to the following. dou r of d e r dou c dou r plus r dou z of d z dou c dou z equal to k v into c. This is our mass transfer equation. So, this is our mole balance, if it is an energy balance involved we could write similar balance except heat of energy will come and dou t dou r dou t dou z terms will come.

What kind of equation is this, it is a partial differential equation and what is the order is 2. So, we need two boundary conditions in two variables r and z. So, let us try to write down these boundary conditions. Now let us start with what is happening at z equal to 0.

What is happening at z equal to 0, z equal to 0 is a symmetric boundary, symmetric plane. So, concentration gradient at z equal to 0 must be 0 in the axial direction. So, we can write our first boundary condition as dou c dou z is equal to 0 at z equal to 0 this comes from the symmetry.

Now, what happens at z equal to h? What happens at z equal to h that is at this point what is happening at that point the gaseous gas is coming out and I do not know what I said let us say that there is a external mass transfer also. So, that we will have a general module and then we can we can simplify it.

So, what should happen the diffusive flux at z equal to h must be the flux at which material is going from the boundary of the catalyst to the bulk, which is k g into c b minus c. This is all evaluated at z equal to h. What about r equal to a? That means, what is happening at r equal to a. The same thing the diffusive flux, because material can go out from here as well as from r equal to b.

So, at both these r equal to a and b the diffusive flux must be same as the bulk the flux from the surface to the bulk of the bulk of the fluid and therefore, we have these four boundary condition.

So, our total mass balance equation plus four boundary conditions is given in this particular manner. So, let us now try to see how we can second part of the problem was to convert this into a dimensionless form the equation should be now dimensionless.

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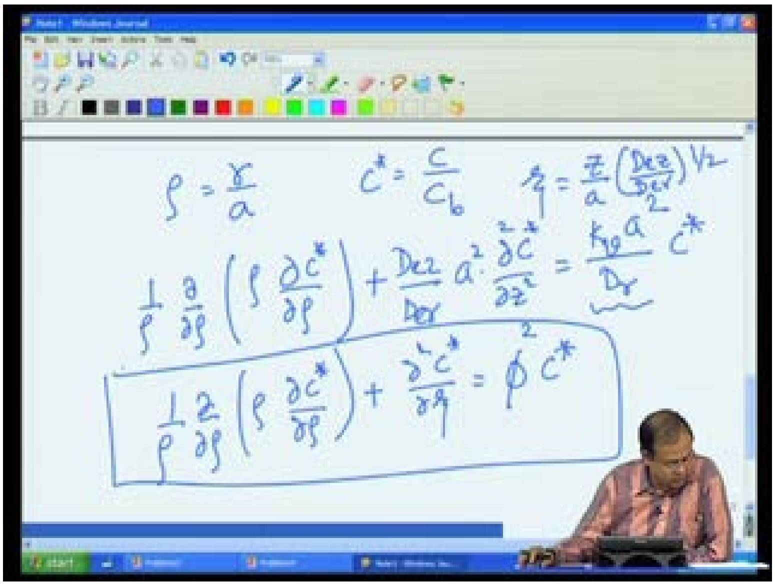

$$\rho = \frac{r}{a} \qquad c^* = \frac{c}{c_b} \qquad \zeta = \frac{z}{a}\left(\frac{D_{ez}}{D_{er}}\right)^{1/2}$$

$$\frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho \frac{\partial c^*}{\partial \rho}\right) + \frac{D_{ez}}{D_{er}} a^2 \cdot \frac{\partial^2 c^*}{\partial z^2} = \underbrace{\frac{k_v a}{D_r}}\, c^*$$

$$\boxed{\frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho \frac{\partial c^*}{\partial \rho}\right) + \frac{\partial^2 c^*}{\partial \zeta} = \phi^2 c^*}$$

So, now let us define the dimensionless quantities namely rho equal to r by r by a and c star equal to c by the bulk concentration and another variable zeta which let me use these two and see how we get that. So, if we use this rho and c star and put it in this mass balance equation for example, we will get the following.

One over rho dou rho of rho dou c star dou rho plus d e z by d e r a square dou c star by dou z, we have not done anything to z yet, so k v a square by d r into c star. So, now we can define dimensionless length zeta. So, that this parameter becomes unity.

So, how do we do that we define raise to half and if we do that then this quantity will become unity and we will get our mass balance equation in the dimensionless form. No, it should be dou square as immediately we recognized that this parameter is something which we had done for a first order spherical catalyst for example, where there was a radius.

So, we can define this as a Thiele modulus, it is a dimensionless quantity phi square c star. So, this is our dimensionless form of the mass balance equation and then we can similarly convert our boundary conditions also in the dimensionless form and I will skip that part.

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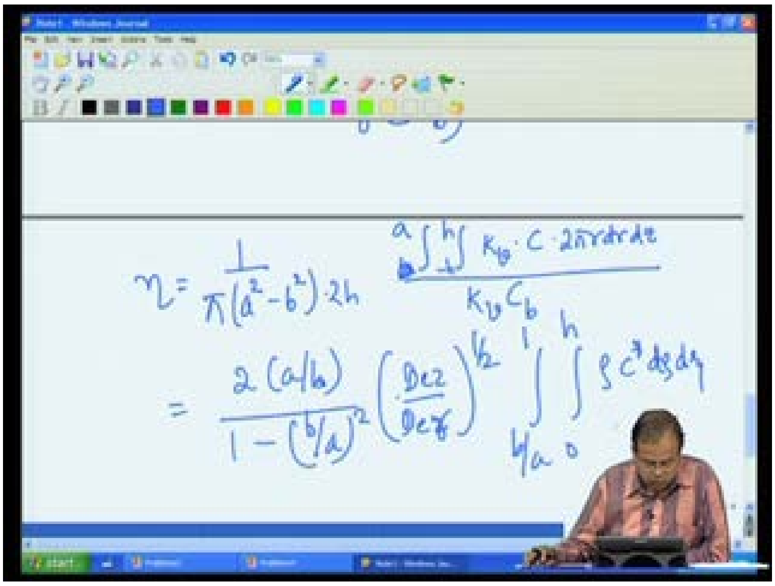

$$\eta = \frac{1}{\pi(a^2-b^2)\cdot 2h} \frac{\int_b^a \int_{-h}^{h} k_v \cdot C \cdot 2\pi r\, dr\, dz}{k_v C_b}$$

$$= \frac{2(a/b)}{1-(b/a)^2}\left(\frac{D_{ez}}{D_{er}}\right)^{1/2} \int_{b/a}^{1} \int_{0}^{h} \rho c^* d\rho\, d\eta$$

Now, let us come to our effectiveness factor. What is our effectiveness factor? It is the observed rate so, one over v integral r d v that is the observed rate, which is varying along the entire volume of the catalyst. So, integral and normalized by the volume that is volume divided by the rate that would have been , if there was no mass transfer limitation; that means, my concentration c is same as the bulk concentration.

Now, for a spherical catalyst what is the volume? The volume is difference between the volumes of the outer cylinder minus the volume of the inner cylinder. So, what is that volume, that volume therefore, eta is what is that volume of the outer cylinder pi a square into h or rather 2 h minus pie b square into 2 h. So, into 2 h that is my volume.

Now, what is this d v, remember we have changes in both radial and axial direction. So, from a to b or b to a from b to a from minus h to plus h k v into c into 2 pi r d r d z. That is the volume d v and what would have been the rate, if mass transfer was not limiting. So, that is k v into c b. So, this is my effectiveness factor. So, what needs to be done is to make this also dimensionless and if you do that we are left with this form of the dimensionless quantity.

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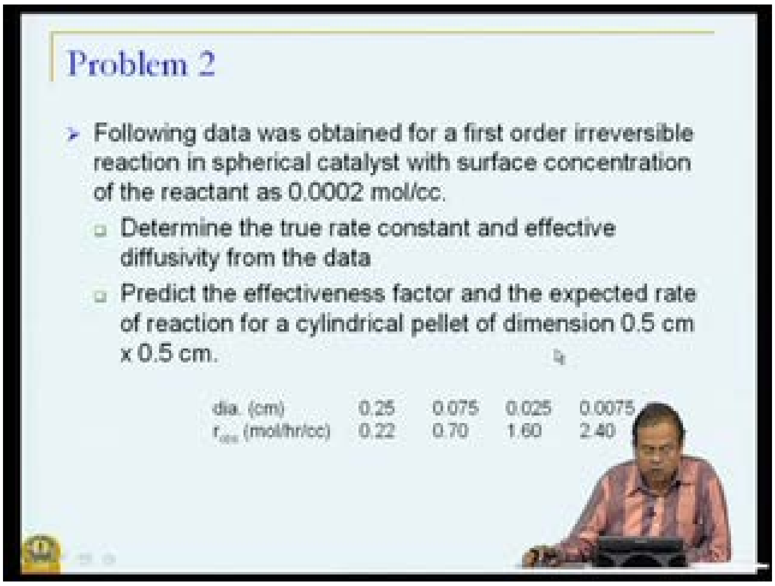

Problem 2

- Following data was obtained for a first order irreversible reaction in spherical catalyst with surface concentration of the reactant as 0.0002 mol/cc.
  - Determine the true rate constant and effective diffusivity from the data
  - Predict the effectiveness factor and the expected rate of reaction for a cylindrical pellet of dimension 0.5 cm x 0.5 cm.

dia. (cm)	0.25	0.075	0.025	0.0075
r_{obs} (mol/hr/cc)	0.22	0.70	1.60	2.40

So, that is our definition of our effectiveness factor, which was what our problem was. Let us look at one more problem. The following data was obtained for a first order irreversible reaction in a spherical catalyst with a surface concentration of reactant as C 0.0002 moles per C . So, the data is given. Data is given, so from this we have to find the true rate constant and effective diffusivity and predict the effectiveness factor and expected rate of reaction for a cylindrical pellet of dimension 0.5 centimeter by 0.5 centimeters.

So, here the experimental data is given you have to the bulk concentration is given. We have to do certain calculations to find out what is the true rate and effective diffusivity. So, this is how we can use our experimental data, because this is our observed rate, which you can always measure by looking at concentration differences diameter, which is size which we know.

So, based on this can we get information about the true kinetics of the process and the estimate of diffusion coefficient, which we saw is an, if modified or effective diffusion coefficient because of this factor. So, let us see how we go about doing this.

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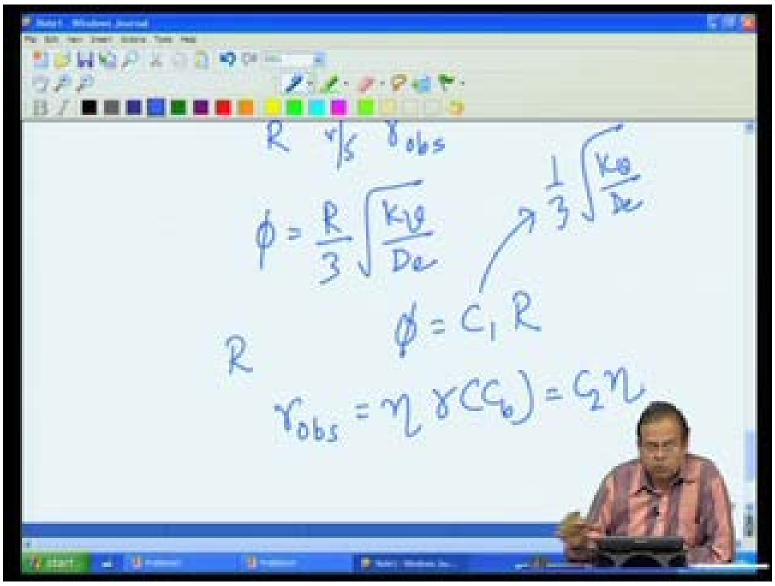

R vs r_{obs}

$$\phi = \frac{R}{3}\sqrt{\frac{k_v}{D_e}}$$

$$\frac{1}{3}\sqrt{\frac{k_v}{D_e}}$$

R

$$\phi = C_1 R$$

$$r_{obs} = \eta\, r(C_0) = C_2 \eta$$

So, what is given to us is the radius diameter; that means, radius versus r observed is given to us. We are also given that it is a spherical catalyst. So, let us define a Thiele modulus for a spherical catalyst. Remember k v and d e, k v is the true rate constant, d e is the diffusion coefficient. Then this is what something, we want to get we do not know what that value is.

So, let us see how we use this information, this is the knowledge we have, this is the information that is available to us to find this quantity. So, I know radius which according to what is our phi is some constant C 1 times radius. What is this C 1? C 1 is nothing, but 1 by 3 square root of k v into d e some constant. Now what is our observed r observed is eta times r at bulk condition, the bulk concentration is also given to us.

So, the rate at that bulk concentration is same whether, we do catalyst in one millimeter, ten millimeter or ten meter. So, that is constant, we can write this as C 2 into eta.

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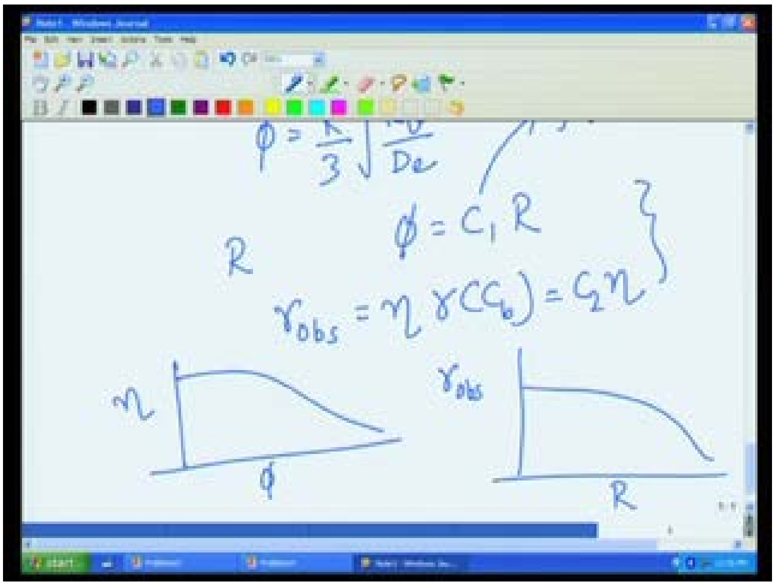

So, now what happens we know that eta versus phi plot is something like this, for a first order reaction. Now we do not know phi, we do not know eta so we cannot plot this, but what do we know? We know r observed this quantity. So, if I plot r observed versus I do not know Thiele modulus, but I know the radius of the catalyst pellet.

So, what do you think should happen? As this two relationship suggest these two axes phi and r are related to each other through a constant C 1. I do not know what that constant is, but that is a constant. Similarly, r observed and eta is related to another constant C 2.

Once again, I do not know what the value of that c 2 is, but I know it is a constant. So, this is nothing, but linear transformation of eta and phi will give you r observed versus r. So, that also qualitatively will have the same behavior and you want to find out what is that linear transformation between the two is.

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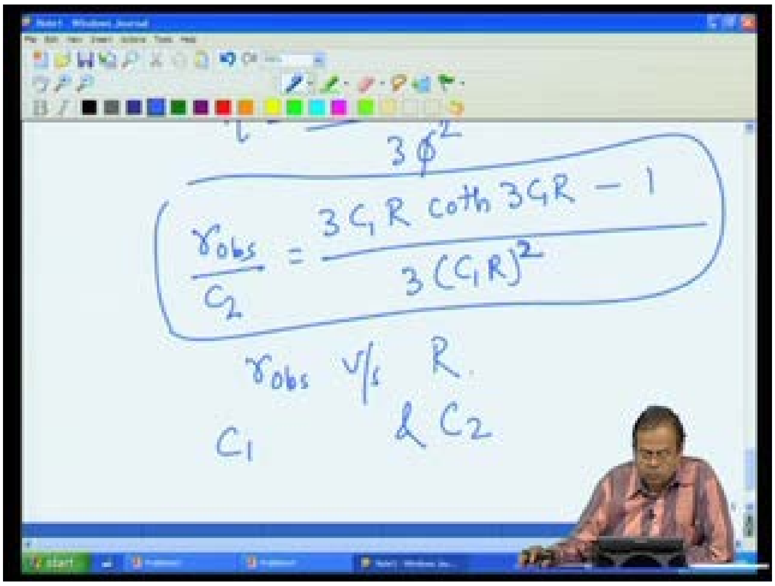

So, now let us rewrite this and see how we can get that, we know for a spherical catalyst our eta is 3 phi coth phi 3 phi minus 1 divided by 3 phi square. So, for eta I am going to put from this particular expression r observed by C 2. So, r observed by C 2 and for Thiele modulus, I am going to put C 1 into r and so if I do that I will get this is equal to 3 into C 1 into r coth 3 C 1 r minus 1 divided by 3 into C 1 into r the whole square.

Now, what do I have? I have r observed versus radius. So, in principal I can do a regression analysis for r observed versus r with this function, this whole function and get value of C 1 and C 2.

Now, in reality if you want to do a good regression analysis, you must have lots of data and we have four data points, since then the unknowns are only two. You would not get the exact estimate, but for class work problem we certainly can get an estimate.

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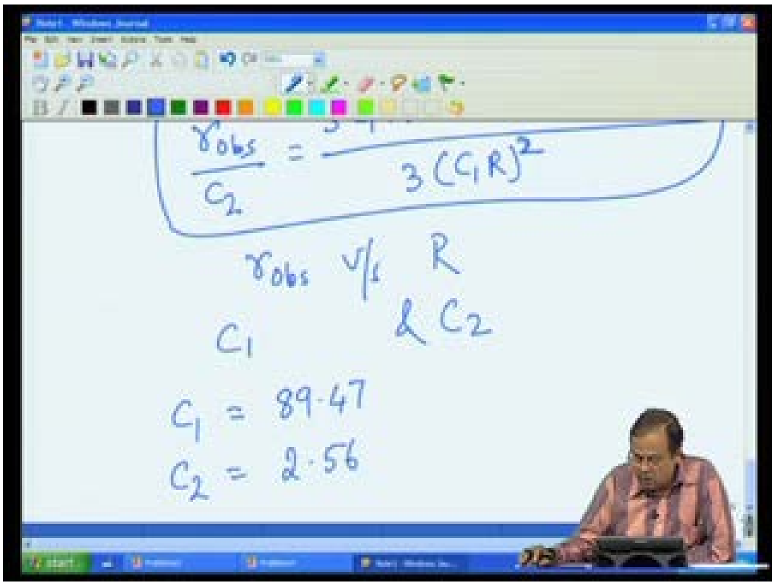

$$\frac{\gamma_{obs}}{C_2} = \frac{}{3(C_1R)^2}$$

γ_{obs} v/s R

C_1 & C_2

$C_1 = 89.47$

$C_2 = 2.56$

So, if we now do a regression analysis between R observed versus R, using this function and then from that regression analysis we will get C 1 and C 2 and that works out to be C 1 is 89.47 and C 2 is 2.56 regression analysis.

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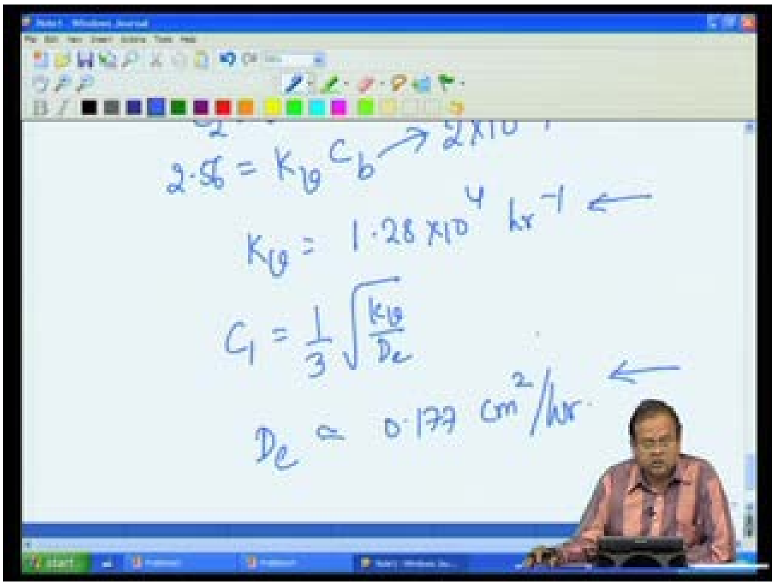

$2.56 = K_v C_b \rightarrow 2\times10$

$K_v = 1.28\times10^{4}\ hr^{-1} \leftarrow$

$$C_1 = \frac{1}{3}\sqrt{\frac{K_v}{D_e}}$$

$D_e \simeq 0.177\ cm^2/hr \leftarrow$

Now, what is our C 2? Our C 2 if you go back our C 2 is r of c b. So, C 2 is r of c b, which according to our module equation is k b into c b. I know my C 2 2.56, I know my c b which is 2 into 10 rise to minus 4 giving rise to k v equal to 1.28 into 10 rise to 4 hour inverse.

What is my C 1? My C 1 is 1 by 3 square root of k v by d e. I know k v, I know C 1, I can calculate D e which comes out to be 0.177 centimeter square per hour. So, this is how we can get estimates of our true reaction rate constant and effective diffusivity given the experimental data of rate at different sizes of the catalyst pellet. The second part of our problem is predict the effectiveness factor for and the expected rate for cylindrical pellet, this was all for spherical pellet.

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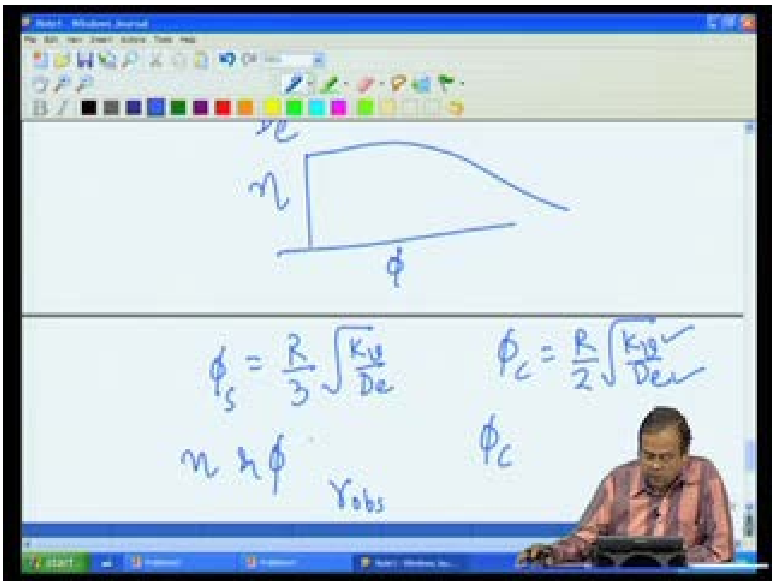

$$\phi_s = \frac{R}{3}\sqrt{\frac{k_v}{D_e}} \qquad \phi_c = \frac{R}{2}\sqrt{\frac{k_v}{D_{e}}}$$

$\eta \sim \phi$ ϕ_c

r_{obs}

Now, how can we predict? If you recall our relationship between eta and Thiele modulus is more or less same or almost identical. If we define our Thiele modulus properly, that is for if I define my Thiele modulus as what we had done, just now for spherical particle like this or this is for my sphere or for my cylinder r by 2 square root of k v by d e, then this relationship is unique.

So, now what can I do? Very simple. I know r which is given as I think 0.5 by the size is given as 0.5 by 0.5. So, R will be half of 0.5 0.25, I know k v I just now calculated, I know d e which also I calculated. So, I know phi c and I know relationship between eta and phi for sphere which I will assume also applies to cylinder because we had seen this.

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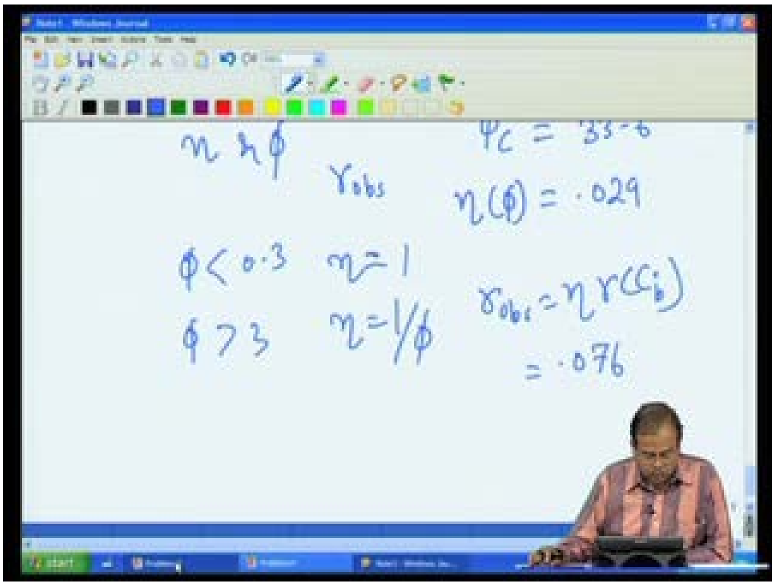

η & ϕ

r_{obs}

$\phi_c = 33.6$

$\eta(\phi) = .029$

$\phi < 0.3 \quad \eta = 1$

$\phi > 3 \quad \eta = 1/\phi$

$r_{obs} = \eta\, r(C_b)$

$= .076$

So, from that we will get observed rate first of all, we will get phi c which works out to be about 33.6. So, at this phi c eta of phi at this value is roughly 0.029. You do not even have to do any calculation, remember this Thiele modulus is much higher than the value of 3.

What is significance? We had seen for Thiele modulus less than 0.3 eta was close to unity for Thiele modulus greater than 3, eta went 1 over phi. So, moment you know phi you can immediately calculate eta. You do not have to use any formula, because this magnitude is an order of magnitude higher than phi equal to 3.

So, we have our solution and then r observed will be eta times r of c b. So, we have all the information and we will get observed rate which works out to be 0.076. Let us look at another problem, I think this one we had seen earlier.

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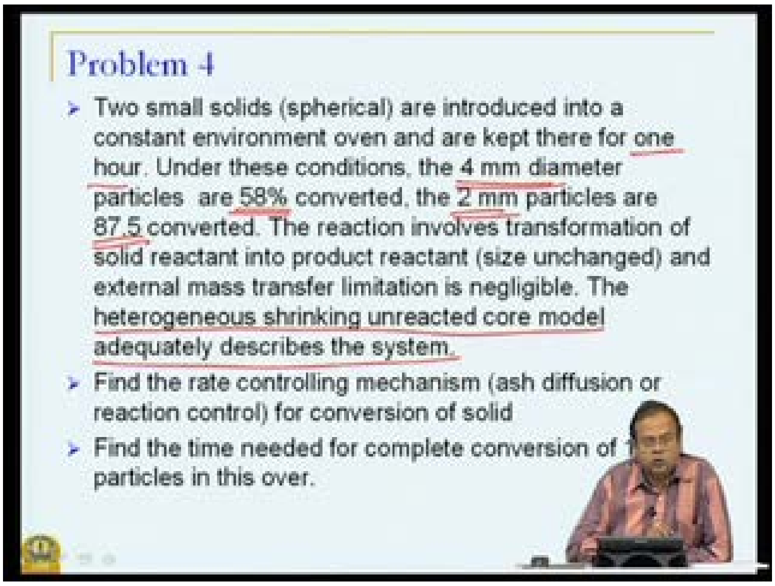

Problem 4

- Two small solids (spherical) are introduced into a constant environment oven and are kept there for one hour. Under these conditions, the 4 mm diameter particles are 58% converted, the 2 mm particles are 87.5 converted. The reaction involves transformation of solid reactant into product reactant (size unchanged) and external mass transfer limitation is negligible. The heterogeneous shrinking unreacted core model adequately describes the system.
- Find the rate controlling mechanism (ash diffusion or reaction control) for conversion of solid
- Find the time needed for complete conversion of particles in this over.

Let us look at this problem, based on gas-solid catalytic reaction. What does it say? It says that two small solids spherical are introduced in a constant environment oven with and are kept there for one hour.

So, this is a piece of information that we have under these conditions 4 millimeter diameter particle is converted conversion is 0.58. 2 millimeter particle it is 87.5. The reaction in once transformation of a solid reactant into product reactant, the size is unchanged.

An external mass transfer limitation is negligible. The heterogeneous shrinking unreached core model is adequate. Find the rate controlling mechanism as diffusion or reaction control and find the time required for complete conversion of particle in this oven.

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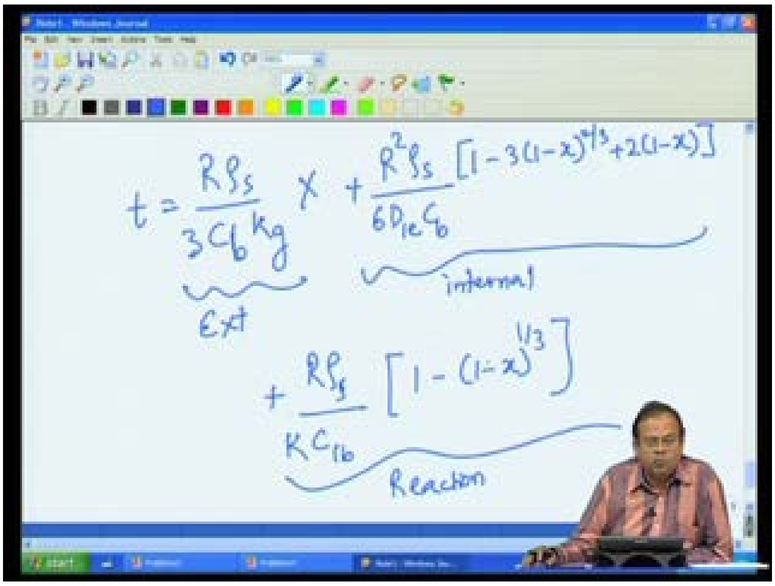

$$t = \underbrace{\frac{R\rho_s}{3C_b k_g}}_{Ext} X + \underbrace{\frac{R^2\rho_s}{6D_{ie}C_b}\left[1-3(1-x)^{2/3}+2(1-x)\right]}_{internal}$$

$$+ \underbrace{\frac{R\rho_s}{KC_{1b}}\left[1-(1-x)^{1/3}\right]}_{Reaction}$$

This is important, because this is given to us. So, we immediately know what is the time required for complete conversion. If we take all the three phenomena that time and this we had seen or you can see these expression into conversion x contribution from external mass transfer plus, what are various terms here r is the radius the initial radius of the particle, rho s is the density of the density of the particle, d 1 is the diffusion coefficient.

So, this is corresponds to contribution due to internal diffusion plus r rho s, rho s is the solid density c b is the bulk concentration x is our conversion, this is if reaction is controlling. So, we have the time required as a function of conversion for a general scenario, when all external mass transfer, internal mass transfer and reaction dominate or play an important role.

Now external mass transfer is negligible here. So, this contribution is 0. So, now we have to examine whether for the data that is given to us. What is that data? we have been given two sizes particles of two sizes and in one hour; that means, in the time one hour what is the conversion for this two different sizes particles. So, we have to find out whether internal transfer controls or reaction controls.

Now, how do we do that. So, let us assume that internal controls or internal diffusion controls, then we will get time as that means, this term is negligible only first term is applicable.

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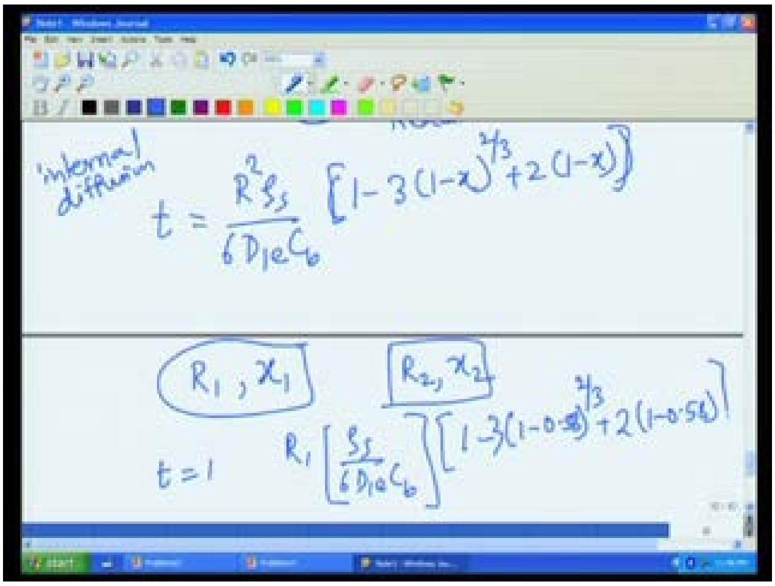

internal diffusion

$$t = \frac{R^2 \rho_s}{6 D_{1e} C_b}\left[1 - 3(1-x)^{2/3} + 2(1-x)\right]$$

$$\boxed{R_1, x_1} \qquad \boxed{R_2, x_2}$$

$$t = 1 \qquad R_1\left[\frac{\rho_s}{6 D_{1e} C_b}\right]\left[1 - 3(1-0.58)^{2/3} + 2(1-0.58)\right]$$

So, r square rho s by 6 D 1 e into c b into 1 minus 3 into 1 minus x two-third plus 2 into 1 minus x. So, this is if internal diffusion controls that means, first and third term are negligible. Then, based on information that is given to us. What is given to us is r conversion. So, two different particles and conversion. So, let us say r 1 x 2 is known to us, r 2 x 2 is known to us and time is same 1 hour.

So, knowing time t equal to 1 hour for r 1 and I will keep these terms rho s, because that is constant, I do not know what that value is should be 1 minus. Let us say this is conversion is this must be and if internal conversion was the same, this must be also r 2 into corresponding same term into one minus, whatever was the conversion there, that is 875 rests to 2 by 3.

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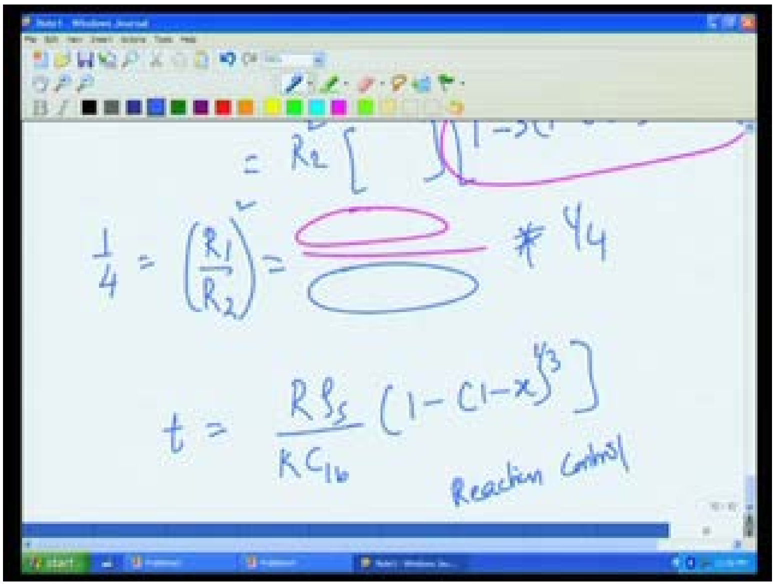

So, if this was correct then, the ratio of the two should be equal, because that is the same one hour. Now it turns out that the ratio of r 1 to r 2. So, what must happen r 1 to r 2 plus 2 into 1 minus 0.875 as it is complete, r 1 by r 2 must be this factor over here So, I will just show it like this divided by this factor over here.

The actual r 1 to r 2 is 1 by 4 r 1 square, actually this square r 1 square by, but this is not 1 by 4 not equal to 1 by 4 that means, diffusion is not the correct. Now what will happen, if I assume reaction is reaction is controlling then I get this.

So, I can do the same exercise r 1 r 2 and it turns out that ratio is correctly matches that means, the reaction control is the correct controlling regime. So, with this few examples we will stop for this session and continue to our discussion on the last module, in this course namely reactor design thank you.