Chemical Reaction Engineering II

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Lecture - 13
Effectiveness Factor and Introduction to External Mass Transfer

Good morning. So, let us continue with our problem like we had stated a problem last time if you remember, okay, it is a spherical particle that we have and there is some data given about a concentration.

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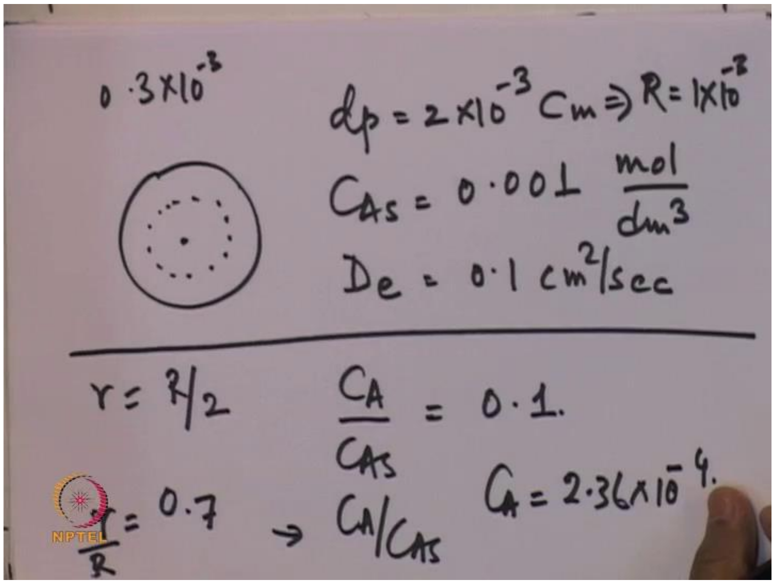

0.3×10^{-3}

$d_p = 2\times10^{-3}\ cm \Rightarrow R = 1\times10^{-3}$

$C_{AS} = 0.001\ \frac{mol}{dm^3}$

$D_e = 0.1\ cm^2/sec$

$r = R/2 \qquad \frac{C_A}{C_{AS}} = 0.1.$

$\frac{r}{R} = 0.7 \rightarrow C_A/C_{AS} \qquad C_A = 2.36\times10^{-4}.$

So, the diameter of the particle is 2 into 10 raise to minus 3 centimeters, okay and the external concentration c a s is equal to 0.001 moles per d n q, right, then it is said that in the diffusion coefficient or effective diffusivity is 0.1 centimeters per second the data given. And moreover it is like also given that at half a distance that is r is equal to capital R by 2, right; the concentration is ah c a by c a s is equal to 0.1, right. So, from this, they have asked what would be the concentration when r by capital R is equal to 0.7 or in other words, if this distance is 0.3 into 10 is to minus 3 centimeters from the external surface.

The radius is radius is 1 into 10 raise is to minus 3, okay, so 0.3. So, remaining would be 0.7. So, r by capital R is 0.7. So, what is c a by c a s, and we have solved this problem. And we arrived at a answer c a is equal to 2.36 into 10 raise to minus 4; how did we do that? Because we know the concentration relation for the concentration profile, okay.

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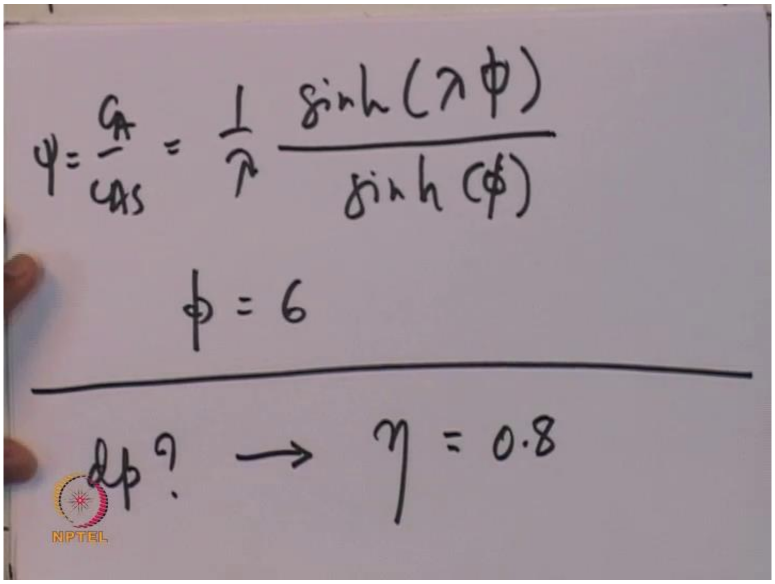

$$\psi = \frac{C_A}{C_{AS}} = \frac{1}{\lambda}\frac{\sinh(\lambda\phi)}{\sinh(\phi)}$$

$$\phi = 6$$

$$d_p ? \rightarrow \eta = 0.8$$

We know the relation for the concentration profile that is c a by c a s which is denoted as i is equal to 1 by lambda, alright, sign h lambda into phi phi that is Thiele models sign h phi, okay. So, from the given data, we can calculate phi which came out to be me 6 and then again we substitute it for the distance lambda dimensionless distance and we calculated c a. So, c a was equal to or ca was equal to 2.36 into 10 raise to minus 4, okay. So that is a quick revision of what we have learned last time.

Now the next part of this problem is that what should be the diameter, okay, then understand this; what should be the diameter so that eta that is effectiveness factor is 0.8, okay. So, it is very so let us try and learn from this, okay; just solve the numerical problem one thing, okay, but at the same time, let us understand what they are trying to say. We can manipulate a diameter of the particle and get an effectiveness factor that we want. What is the importance of effectiveness factor? Effectiveness factor is going to decide a rate, because actual rate is nothing but effectiveness factor into the intrinsic rate, okay.

Now if the effectiveness factor is close to one that means there is no pore deficient resistance. So, I can manipulate I can design the catalyst particle have the catalyst particle size in such a way that the deficient resistance is negligible, okay; that means effectiveness factor is close to 1. In this case, they are asking no no do not for one that will too much; I will tell you why, okay, but then 0.8 is good enough, okay. Let us see what happens, but before that, we need to understand, okay, what is the effectiveness factor, otherwise, like for the given diameter, okay. For the given diameter, what is the effectiveness factor?

If the effectiveness factor is already 0.9 or 95, then there is no point in bringing it down, okay; anyway they have asked it, then we have to solve it, alright. But it is quite likely that effectiveness factor is much lower compared to pointed and that is why we need to play with the diameter, okay. So, in the first part of the question, we just looked at a concentration, right, from the concentration profile. We calculated the Thiele models, okay, but let us try and understand what is the effectiveness factor in the first part itself and then we will see, okay, how to manipulate or how to get a value of effectiveness factor to be o.8, so that there should be a required diameter for it, alright, fine. So, what is the effectiveness factor in the earlier case when the diameter is 2 into 10 raise to minus 3 centimeters which is given rather, okay.

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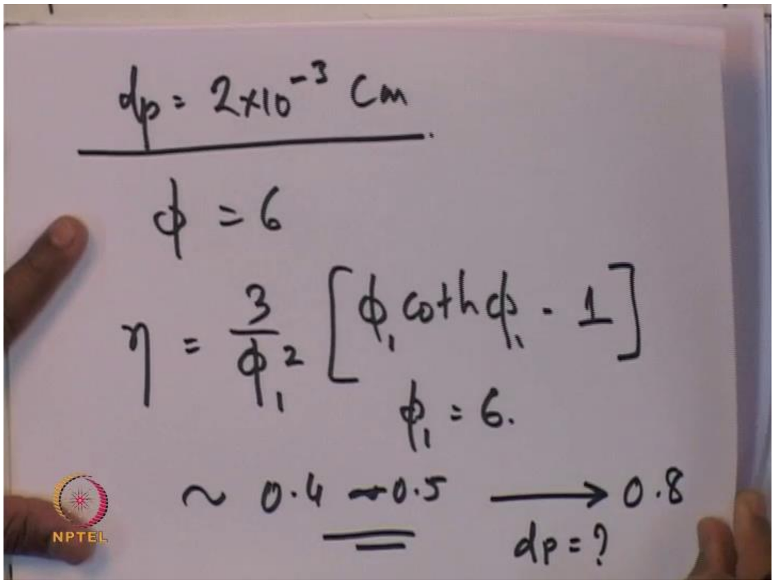

$$\underline{d_p = 2\times10^{-3}\ \text{cm}}$$

$$\phi = 6$$

$$\eta = \frac{3}{\phi_1^2}\left[\phi_1 \coth\phi_1 - 1\right]$$

$$\phi_1 = 6.$$

$$\underline{\underline{\sim 0.4 \to 0.5}} \xrightarrow[d_p = ?]{} 0.8$$

So, d p is 2 into 10 raise to minus 3 centimeter is the earlier case; phi is 6. So, eta is equal to 3 divided by phi 1 square phi 1 cot h phi minus phi 1 minus 1; we know this, okay. We know this. Now you substitute phi 1 is equal to 6 here, okay; you are going to get a value which is much less than 0.8, you can verify that, okay. It would be of the order of 0.4 to 0.5, okay that low. I have not calculated it but you can do it yourself or it can be somewhere close to this range, right. Now this value is lower so the rate is lower, but i am not happy with this rate. Look at a particle diameter 2 into 10 raise to minus 3 centimeters, right, 2 into 10 raise to 1 centimeter is this much, okay, 2 into 10 raise to minus 3, okay; 0.1 centimeter is 1 millimeter.

So, this is going to be less than millimeter small it looks like powder, okay, but still the effectiveness factor is 0.4 to 0.5 which is something that I am not happy with, okay. So, I need to play with a particle diameter; can I play with the diffusivity? Now I have prepared a catalyst, okay; the diffusivity depends on the pore diameter. It depends upon the porosity; it depends on the tortuosity; it depended on the constriction factor remember. So, with this, now I cannot play with that, okay. I have prepared a catalyst.

Now only thing that I have played with is a diameter; I can grind that catalyst I mean grind that catalyst, okay, but I cannot change the internal morphology. So, diffusion coefficient cannot be changed. The only thing that I can change and get higher effectiveness factor is the diameter length, okay. Always remember that diameter is something that you can quickly play with, right. I can always grind the catalyst if I want to reduce the value of diffusion resistance or increase the value of effectiveness factor; that is what we are learning through this problem, okay.

It will not take much time to numerically solve this problem, but I am trying to convey, okay, like what is the meaning behind all this, okay; that is more important, alright. Now if I want to take this value of effectiveness factor to 0.8, this is d p I need to vary, okay, fine. So, in order to vary d p, what do I need to do?

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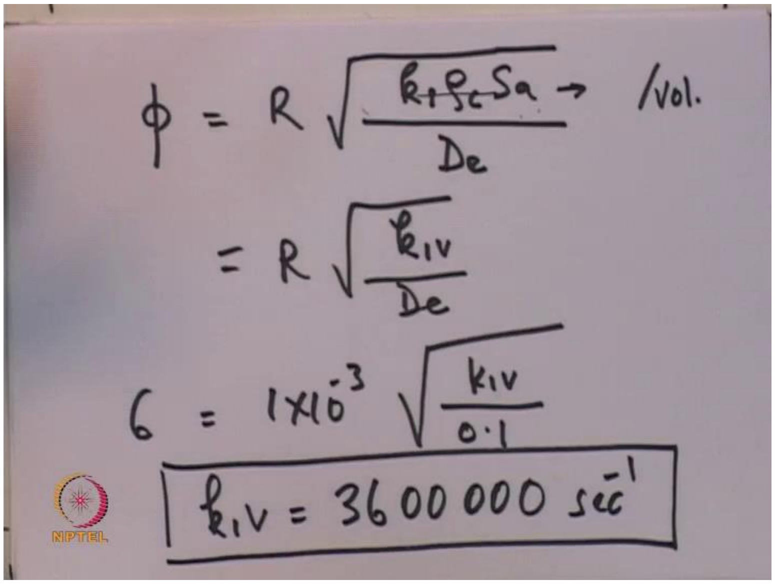

$$\phi = R\sqrt{\frac{k_1 \rho_c S_a}{D_e}} \rightarrow \text{/Vol.}$$

$$= R\sqrt{\frac{k_{1v}}{D_e}}$$

$$6 = 1\times10^{-3}\sqrt{\frac{k_{1v}}{0.1}}$$

$$\boxed{k_{1v} = 3600000 \text{ sec}^{-1}}$$

First of all, what is phi? Phi is r root k 1 rho c s a divided by d e; I do not need to by heart this equation. I know the proportionality like see if you have increased r, then resistance is going to increase. If I increase diffusivity resistance, it is going to decrease, okay, and relatively if I increase the value of intrinsic rate constant, again the diffusion is going to important, okay, if the resistance is going to be important. So, that is how I remember this equation, and what is this numerator? Numerator is nothing but the rate constant per unit volume, okay; it is per unit volume; we already looked at that, right.

So, this is nothing but a rate constant. Let us not get into detail; this is a rate constant, fine. Now let me just denote this is as r k 1 v divided by d e, okay, why v because per meet volume the numerator. What do I know in all this? Six is equal to 1 into 10 raise to minus 3 k 1 v divided by the diffusivity or diffusion coefficient that is 0.1. So, I get an intrinsic rate constant which is 3600000, okay. You can do this numerical calculation and check, okay. What would be the unit? It is the first order reaction; unit is per unit volume, okay, the volumetric rate constant. So, it is going to be secant inverse; we have already seeing that.

So, I have determined a value of intrinsic rate constant which is not going to change; this value of rate constant is not going to change even if I change diameter, okay. So, if I want higher values of effectiveness factor, I am going to change the diameter but rate constant is going to remain the same, remember that, okay, fine. So, let us go ahead.

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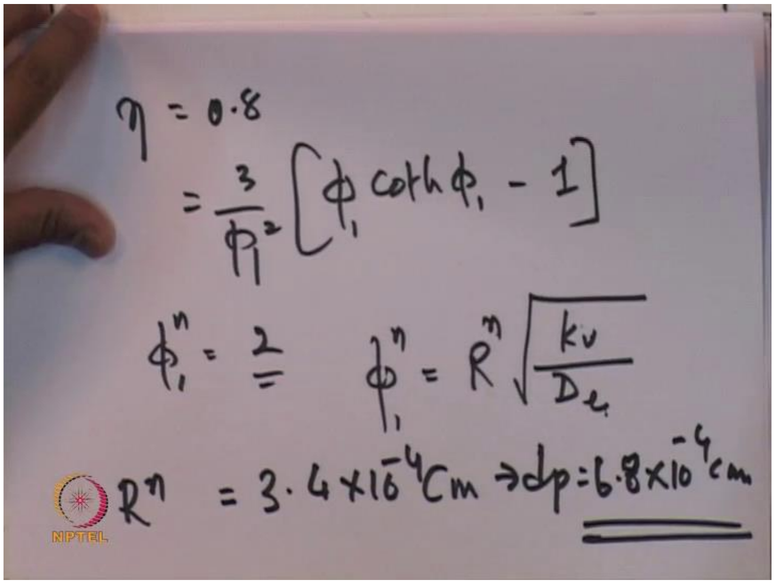

$$\eta = 0.8$$

$$= \frac{3}{\phi_1^2}\left[\phi_1 \coth\phi_1 - 1\right]$$

$$\underline{\underline{\phi_1^n = 2}} \qquad \phi_1^n = R^n\sqrt{\frac{k_v}{D_e}}$$

$$R^n = 3.4\times10^{-4}\,\mathrm{cm} \rightarrow \underline{\underline{d_p = 6.8\times10^{-4}\,\mathrm{cm}}}$$

Now I want effectiveness factor to be 0.8 which is nothing but 3 by phi 1 square 51, right cot h phi 1 minus 1. So, for 0.8, phi 1 becomes it is got be less or more? It is going to be less, why? Because effectiveness factor is increased, the phi 1 value is going to go down, okay, right. So, phi 1 becomes 2, just check that, okay. When I substitute when I do trial and error, just assume the value of phi 1 get this. See whether it is equal to 0.8 or not? If it is not, then go and change the value of phi 1; it is a trial and error method, okay and get value of phi 1.

Now with this value of phi 1, now again I go back to the expression for phi 1 is equal to r root of k v divided by d e. What is that I do not know in this? Of course, this is a new value of phi 1, okay; earlier it was 6. So, I say phi n new value, okay. So, I will have a new r. These two are not going to change because d depends on the catalyst morphology pore diameter and inside structure, and this is again something to do with the intrinsic rate constant, okay, which may have absorption desorption also like what we have seen before.

So, these two that is k v and de are not going to change, okay; only r is going to change such that I have a new value of phi 1, okay. So, for the new value of phi 1, you must substitute for k v d e and all, okay. This is not r raise to n; this is new r, okay, just do not get confused. This is superscript and not the index, okay. So, the new value of r, you must substitute for phi and k v that I have calculated 36 whatever, 1000 or lakh, okay and diffusivity. I am going to get r is equal to 3.4 into 10 raise to minus 4 centimeter which says d p is equal to 6.8 into 10 raise to minus 4 centimeter. So, this is my answer.

So, what is happening? Look at this diameter and the one that was giver earlier, okay. The diameter given was 1 into 10 raise to minus 3. Now the diameter that I have calculated is 6 into 10 raise to minus 4. So, diameter has gone down further, okay, and that is the reason I am able to increase the effectiveness factor. So, that is the meaning of, okay. So, I am playing with the diameter to increase the effectiveness factor. In general, if I just do a reaction at different diameters and calculate the rate for a given concentration.

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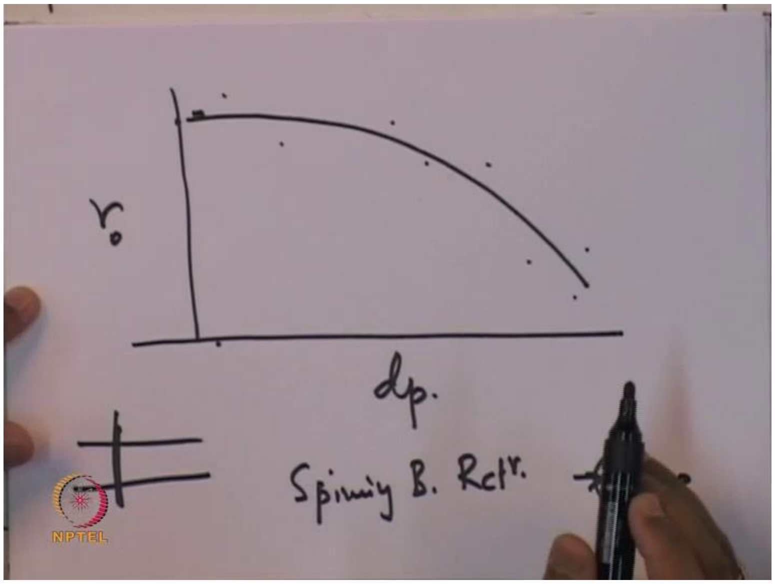

Then the graph is going to be like this in general; I am not talking about this. Now the problem is solved, okay. Now I am talking about a general case a diameter of the catalyst particles and a rate at a given concentration, so say initial rate or inlet rate. You know how to measure this rate. I am doing an experimental laboratory, say; I am using a differential reactor. I am probably using a spinning basket reactor, okay; we already spent some time discussing what is spinning basket reactor. I may be doing experiment in a celery reactor, okay. I am calculating the rate at given concentrations throughout, okay.

I am just changing the practical diameter, okay. So, what kind of behavior I expect here? You plotted on graph possible, okay; what will I get, what kind of relation will I get? This relation is going to be quite similar to the relationship between eta and phi, okay, why? Because the diameter has something to do with the phi and the rate observed has something do with the value of eta. So, the relation is going to like this. So, at lower diameter, you are free of internal diffusion resistances, okay.

So, I get maximum rate and as I go on increasing the diameter, the molecules have to travel or diffuse over a long distance long path, okay because of which the rate is going to go down, the resistance would increase, okay; that is why it is going down; that is the meaning of it. So, if somebody does experiments and give you the data like this, okay; you should know the meaning of that. And, of course, remember all this rate is for a given concentration, and this is what I have observed for different diameter. It is not changing anything else only the diameter. In that case, I see something like this means definitely there is a possibility that diffusion resistance is playing an important role, okay.

I am using a word possibility, okay. Now what is that with why will the rate get effected because change in diameter; here you know the reason, okay. But is that the only reason? If I change the diameter and the overall rate is changing, is there any other possibility. Now what have we looked at so far; adsorption, chemical surface reaction, desorption and internal diffusion, okay our reactant end product. Apart from that, this is something else, okay; that will play the important role in the overall rate or govern the overall rate possibly. You already mentioned about it but not discussed so far in detail, it is the external mass transfer resistance, okay.

External mass transfer resistance which has nothing to do with the particle morphology, nothing to do with the pore diameter with that, nothing to do with the internal structure of the particle, okay; it depends on something that happens at the exterior surface and in the belt, okay. So, we will see that in detail now, okay, but then before that just remember, okay, probably I am not stated it explicitly that I am talking about this rate constant every time intrinsic rate constant say here or wherever I have used the expression k c a and all; that k here I have just used it say for first order reaction r a is equal to minus k c a or if for n th order reaction, it can be c a raise to n.

Now this k of this expression I have used it as a normal rate equation, but sometimes it can be complicated or it says it can have something in the denominator as well, okay, why? That will take care of the adsorption terms; that will take care of the Langmuir-Hinshelwood mechanism, Eley-Rideal mechanism, okay. So, I have not considered it deliberately because then our derivations would become difficult and then interpretation is a problem. So, I have considered very simple case whether rate is given by k c a and that happens, okay, even if you have Langmuir adsorption predominant there; when does that happen?

I told you like if you have very high temperature if you have very high temperature then the adsorption is insignificant. So, the denominator becomes 1, okay, and then the expression boils down to a form of a normal rate expression that is r is equal to minus r a is equal to minus k c a raise to n. So, always remember that whatever analysis we have done here is but considering a simple equation but there is a possibility that you may have adsorption constants, desorption constants of the species involved, okay. In this particular expression if we really want to get very close to reality, okay; right now the purpose is to understand it.

So, that is the reason we have used a very simple equation, okay, alright, okay. So, there are so many problems in the assignment sheets or even at the end of text books like Fogler, Levenspiel and all, you should attempt and solve this problems. This is where we are closing this chapter of internal diffusion, but anyway we will be referring to that because it is not that like once studied and then forgotten, because it will come again and again later in out discussion whenever we try and design a reactor, okay, alright.

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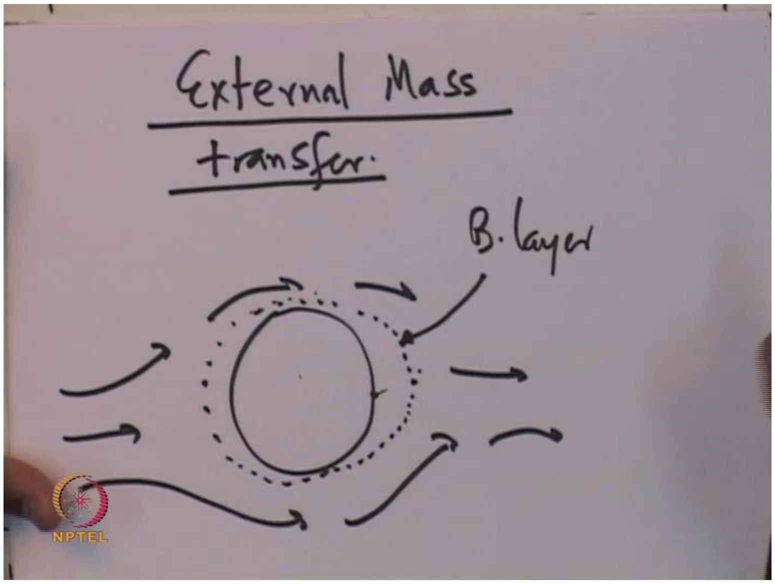

So, we will talk about external mass transfer now. It is a different phenomenon or rather in a step than reaction, adsorption, desorption and internal diffusion. What has happened? External as the name says it is external mass transfer, okay. So, you have a particle and the fluid is flowing over it; this is a catalyst, particle, okay. Now what is likely to happen at the external surface of the particle? It is fluid dynamics non erased, okay. It tells you there is a boundary level here; there is a boundary level slightly non-spherical in nature because of flow patterns. Here it is slightly thicker compared to it.

Of course, this can be equal here, whatever, okay. Now how did you find the boundary layer? How do I define the boundary layer? I define the boundary layer is a thickness of layer in which the velocity is changing, okay. The velocity here near the solid surface is ideally zero; there is no slip, right, and the velocity would go on increasing and will become almost equal to the velocity of the bulk that point, okay. And that particular thickness at which it becomes the same 99 percent of the external because getting it exactly equal will be a problem, okay.

So, getting 99 percent equal, okay; what is the length, okay. That is the length or thickness of the boundary condition. We define it for momentum balance momentum transfer, right; based on the velocity that there is another boundary layer for mass transfer, just similar like your velocity is changing here, right. In the case of component concentrations, there will be a concentration changing here; why is it happening? Because this layer is stagnant or close to a stagnant layer, okay; that is why the concentration will change. The concentration here may not be same as concentration here and that has great implications on the reaction rate, okay.

So, far we have been assuming that the concentration at an exterior or external surfaces, okay, of the particle is same as the concentration in the bulk. C a b is equal to c a s, right. So, far we have not really looked at difference between these two but now we are going to look at a possibility that there is a resistance offered by the external surfaces; the boundary layer is thick enough, so that the concentrations are different. C a b is not same as c a s; c a b is bulk concentration; c a s is the surface concentration, okay. This is because the resistance offered by that boundary layer, okay. So, the concentration is going to increase. So, typical profile in the boundary layer of the concentration is this, okay. This is the concentration boundary layer; earlier I mention about the velocity boundary layer, okay, momentum balance, right.

Now I am talking about the concentration boundary layer, okay. Now let us make certain assumptions and try and quantify the resistance, okay. Now this boundary layer thickness is not very large, okay; in fact, it is very very small compared to a particle diameter most of the times, okay, right. And this boundary layer if we look at a particle, particle is very big, okay and I have a small boundary layer around it. So, at any given point, the curvature can be neglected as far as this boundary layer is concerned.

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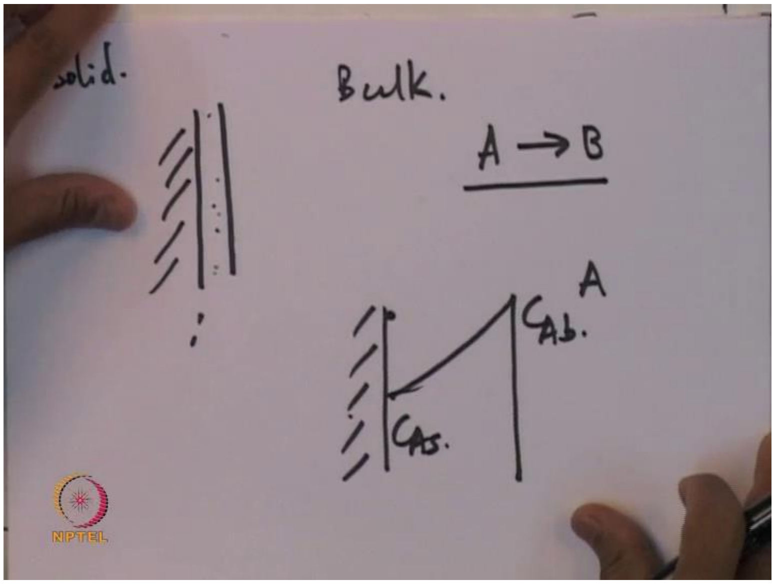

So, I can say that I have a particle, okay, and there is a boundary layer. Not it is quite possible like you have something like this, the curvature will start. So, this is surface; at given point, I can assume it to be flat, and this is the boundary layer. Now this is an assumption that, okay, this boundary layer is stagnant enough and whatever resistance offered by the entire this is where you have bulk, right, and this is where you have a solid. So, whatever resistance on this side, okay, for the mass transfer to take place is offered by this bulk, the condition here may be velocity, whatever okay, the Reynolds number and all that.

So, that particular condition is going to offer certain resistance, okay, and that resistance we are going to assume that that is concentrated in this boundary itself or it is called as filmed, okay. So, all the resistance is concentrated in the filmed; this is a very hypothetical case, okay that I have a film that takes care of all the resistance. So, in terms of a concentration profile, now it looks quite it becomes very easy for the analysis, okay. You have a film; in this the concentration is going to change; how it is going to change? We will see but there is one concentration here, and there is one concentration here.

Now for a reaction to take place, say, a is going to b. So, a is sitting here in the bulk. Now a is going to diffuse through this film and go here, and b is going to come out; of course, inside you have pore diffusion, adsorption, desorption that is occurring, and then b is coming out. So, if a has to transfer from bulk to here, the profiled has to be like this, okay and for b to be other way round. So, let us consider a reaction a going to b, alright; let us consider a reaction a going to b. This is the reason why we are considering this reaction as the first step, okay.

If you have a non-equimolar reaction, you have some different things to be considered, but let us now talk about a simple single reaction which is the assimilation reaction equimolar reaction a going to b, okay. So, a has to diffuse through this layer and go there to the surface. Inside you are already seeing what is happening once it is here, okay; this is you are c a s your c a s, and this is c a b, right. Now I need to know the concentration profile inside; what is the nature of this concentration profile, okay. Whether it will be straight, linier, nonlinear. So, let us try and look at this.

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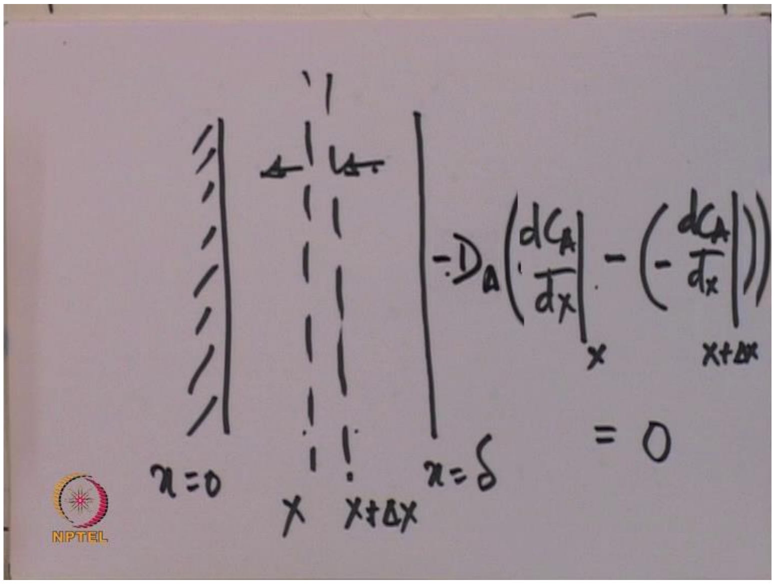

And it is simple; you have already done this type of exercise for inter particle diffusion, okay. So, let me consider a differential element like what I did before also but now it is going to be relatively easy because I do not have spherical coordinates and working Cartesian coordinates, okay. So, this is at x is equal to 0, and this is at x is equal to say delta. So, delta is the thickness of the film. So, this is x plus b x and this is x, right, and diffusion is going to take place in this direction, okay this direction for a; for b it will be opposite.

Now can we write equations here for the flux. So, flux at x, say, d a minus d c a by d x at x minus d c a by d x at x plus d x, right, flux here minus flux here. Why minus sign because d c a by d x is negative; flux has to be positive, okay. So, flux here minus flux here is equal to what? Earlier, what did we do? In the case of inter particle diffusion; there was some reaction that was occurring here. So, coming in minus going out plus reacted is equal to zero, right, but now we have going out coming in; there is no reaction. Reaction is taking place here and not here, okay. It is the only nonreactive mass transfer that is taking place, right. And now if we simplify this for d x it is going to zero, what you get is a very simple equation.

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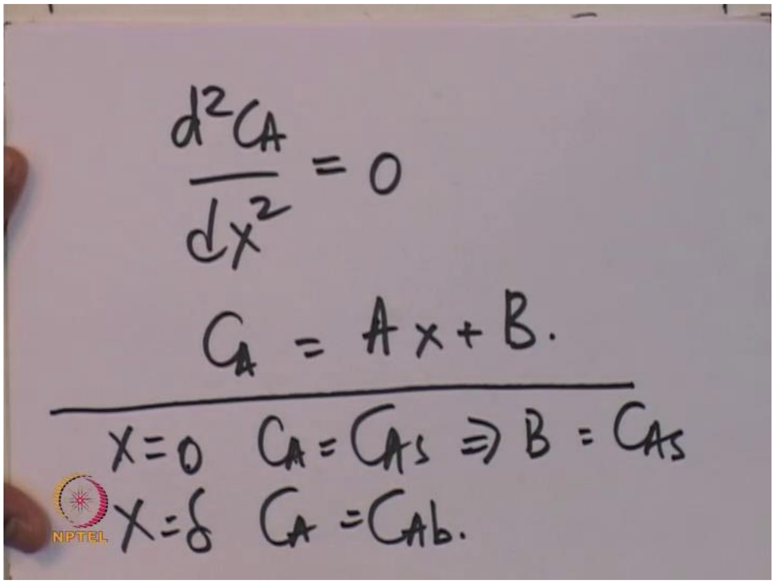

$$\frac{d^2 C_A}{dx^2} = 0$$

$$C_A = Ax + B.$$

$x = 0 \quad C_A = C_{As} \Rightarrow B = C_{As}$

$x = \delta \quad C_A = C_{Ab}.$

A second order differential equations which has a solutions and now we will determine a and b by applying proper boundary conditions; what are the boundary conditions? X is equal to 0, c a is equal to c a s, x is equal to delta, c a is equal to c a b, right. So, determine the value of a and b. So, use this boundary condition x is equal to 0, c a is equal to c a s. So, that implies b is equal to c a s. So, let us calculate the value of a.

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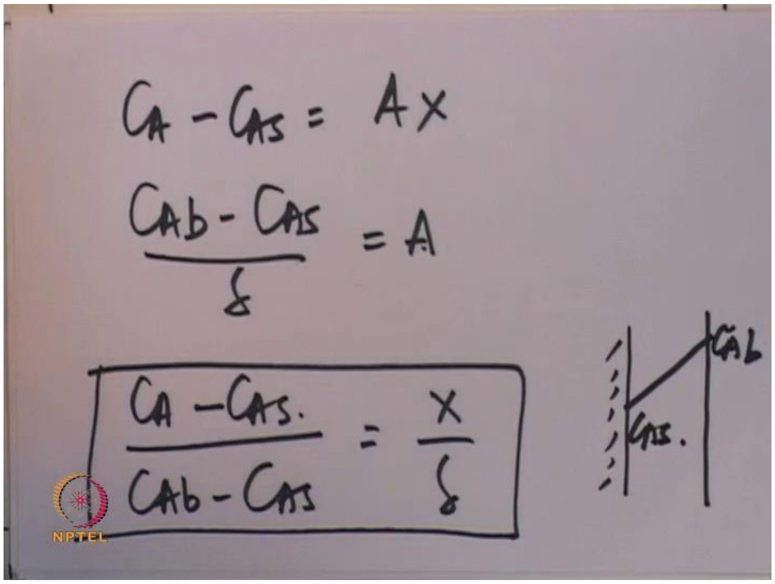

$$C_A - C_{AS} = Ax$$

$$\frac{C_{Ab} - C_{AS}}{\delta} = A$$

$$\boxed{\frac{C_A - C_{AS}.}{C_{Ab} - C_{AS}} = \frac{x}{\delta}}$$

So, c a minus c a s is equal to a x; for x is equal to delta c a is equal to c a b. So, c a b minus c a s by delta is equal to a, and if you substitute now, now this a and b if you substitute here, okay, what I get is c a minus c a s dived by c a b minus c a s is equal to x by delta. So, what does it say? It is a linear profile inside; it is a linier profile inside, okay, and we know the boundary conditions. And this is a delta; the slope is known, right. So, it is a linear concentration profile that makes my exercise quite easy, okay. So, it is you have c a b c a s, right. Why I am doing all this? Because I want get a rate; I want to get a flux.

See mass transfer and diffusion if I want to get a overall rate, I have to go through the flux equation; flux multiplied by cross section area is going to give me the rate, okay. For reaction, we already know, okay, r is equal to k c a and all that; that is the rate, but that depends on the unit of k whether it is per unit volume, per unit area and all that. There is so many possible units, okay. So, be careful about units every time, alright.

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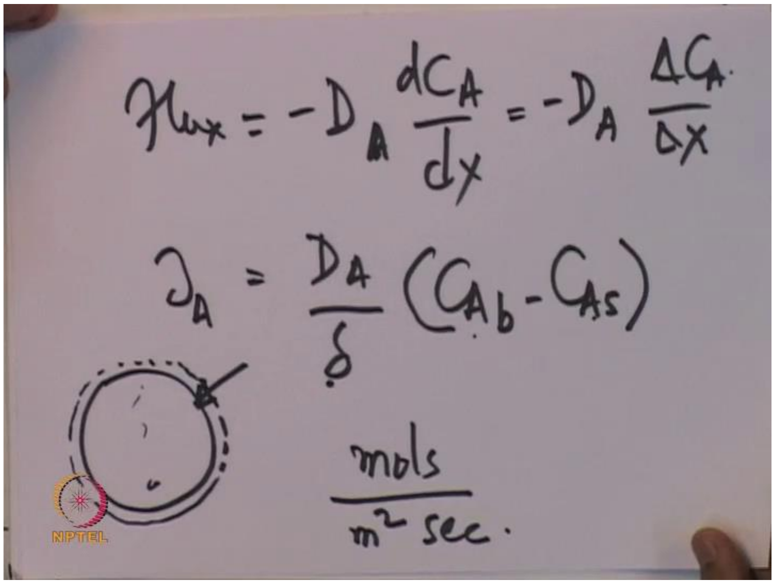

$$\text{Flux} = -D_A \frac{dC_A}{dx} = -D_A \frac{\Delta C_A}{\Delta x}$$

$$J_A = \frac{D_A}{\delta}\left(C_{Ab} - C_{As}\right)$$

$$\frac{\text{mols}}{m^2\ \text{sec}}$$

Flux is equal to d a, right. I am not using effective deficit here as it is a normal deficit in the bulk, okay, diffusivity into d c a by d x. This is going to be linear. So, substitute for this. So, this is going to be d a by delta, alright, into c a b minus c a s, right know; delta x is equal to delta, right, and delta c a is c a b minus c a s linear. So, this is a flux; what is unit? Moles or kilomoles per meter square secant per unit cross sectional area, area for flux. Which area are we talking about by the way? We talked about an area before also an inter particle diffusion, but do not confuse that area with this area, not the area inside.

It is the area here which is almost equal to the external surface area for the mass transfer to take place. So, this is that area cross section are other cross section area for the flux flux, okay. So, here that area is nothing but the particle external surface area because that is where the mass transfer is occurring, okay, but let us keep the same units, right, now okay and go ahead, alright. So, before we go ahead, now this flux is equal to normally it is denoted by j a, okay; it is denoted by j a. This one important assumption that we have made and not assumption rather, we have, right; we call this as assumption because we say that this a going to b reaction. That means it is an equimolar reaction. It is an equimolar reaction.

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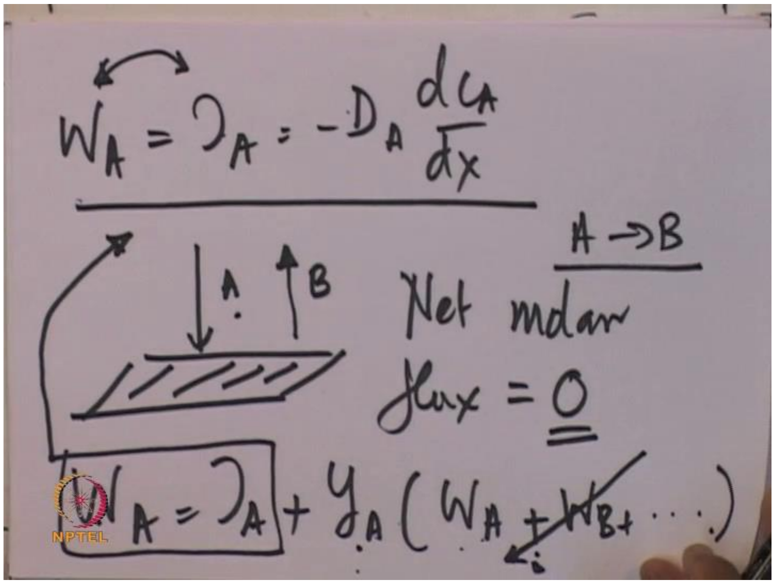

That is why we have written the equation for flux as j is equal to d a d c a by d x; this is fine, okay, but we have equated it equal to w a normal. This happens when you have there are many situations possible. Now you have this surface on which a is going, okay. There is a reaction that is taking place, b is formed. So, b is diffusing back. What is the net flow? It is a queue in a reaction. So, the net molar flux is zero here very important because how much we are going in same amount is coming out internal moles, right; that is why this is equal to this very important. You might have learnt that in basic theory of mass transfer, okay. W a is equal to j a; otherwise, w a is equal to j a plus what? Y a the moles faction w a plus w b plus whatever total.

So, this is net flux; if it is going to be significant or finite, then w a is not equal to j a, but in this particular case for equimolar reaction a going to b, right, this net flux there will be signs for this plus minus whatever and then there are no other components. W a becomes equal to w b but negative sign. So, this become zero and that is why I have w a is equal to j a; this is very important. Again I want to avoid complications; that is why I am considering a going to b reaction, okay, but once you understand this well, it would be easy for you to rather extend it further or more complicated cases.

Here idea is to rather how to incorporate the external mass transfer resistance; how to show the importance of external mass transfer resistance in the overall rate equation, okay? So, that is the main motivation; that is why we are considering a very simple reaction, okay. This will happen w a equal to j a will happen for other cases also. Even if the net flux is finite even if the net flux is finite if y a is zero. So, you have a very dilute solution, then again neglect this, okay, right. So, w a is equal to j a happened in the case of equimolar reactions. It happen in the case of dilute solution as well, okay.

But, otherwise, for non-equimolar reactions or suppose your medium is stagnant, otherwise, there is no equimolar diffusion that is taking place; it is only the mass transfer. There is no one reaction taking place. In that case, we have to be careful, okay; you just remember that, fine. So, let us go ahead.

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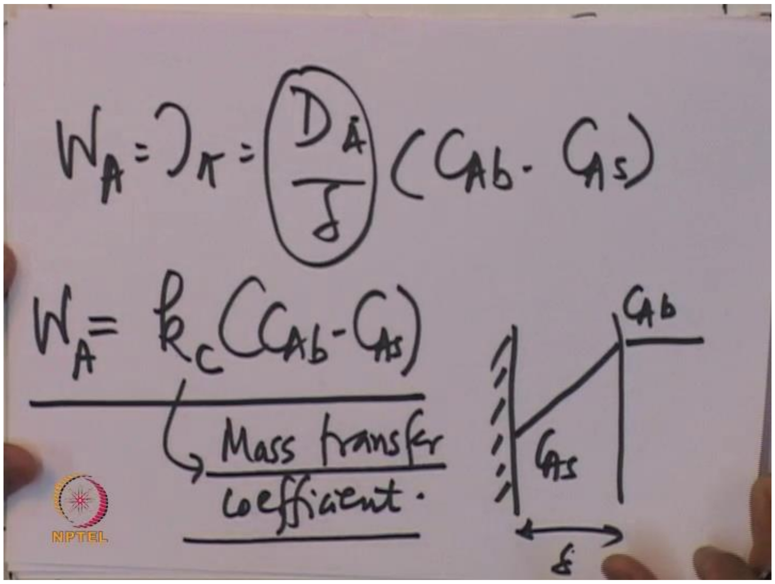

$$W_A = J_A = \boxed{\frac{D_A}{\delta}}(C_{Ab} - C_{As})$$

$$W_A = k_c(C_{Ab} - C_{As})$$

Mass transfer coefficient.

We have j a or w a is equal to j a is equal to d a b y delta c a b minus c a s constant in the bulk. The concentration varies only in the film hypothetical film a stagnant film, okay; that is what we are assuming, okay. Now this particular parameter d a by delta is called as mass transferred coefficient k c; let us denote it as k c, alright. So, w a is equal to k c into c a b minus c a s; again this is flux moles per meter square secant, and this is called as mass transfer coefficient. If you have already learned this probably, okay, mass transfer coefficient depends on diffusivity while diffusivity and delta film thickness.

So, let us spend some time understanding what it this film thickness and all, okay. This is the film thickness, right. Now this film thickness depends on which factors this depends on; what is the condition here, okay. If you have intense agitation, the boundary layer thickness will go down. The value of delta is going go to down; the film thickness is going go to down intense agitation, okay. It depends on the properties also; it is a viscosity, density and diffusivity as well, okay. So, we will talk about correlations for calculating k c later, okay. Let us first complete our analysis when the reaction is taking place, how to incorporate the effect of k c, okay, right.

How to calculate k c; we will see later or look at correlations and all later. But right now let us try and put this in our rate equation in the overall prospective, okay, where you have so many things happing, alright, fine.

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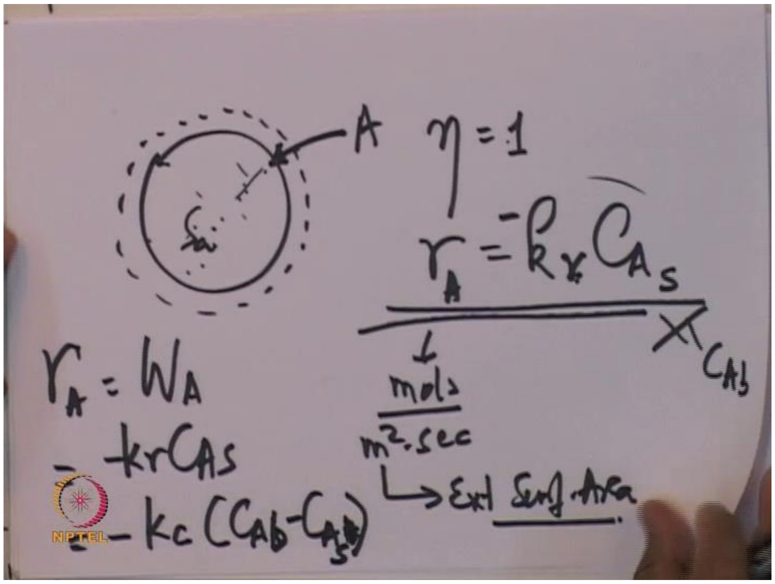

I have a catalyst particle; there is a resistant here. I am not going to neglect it now like what I did before, okay. And a is going here, okay. Once it reaches here, what is the rate? The rate is given by eta into intrinsic rate, okay. Once it reaches here but before it reaches here, it is experiencing some resistance. So, these two are again the steps taking place in series, okay, and relative importance is going to decide, okay, which is the governing state which is the rate determining state and all that; again the same logic, fine.

So, let us assume that eta is equal to 1; let us assume that eta is equal to 1, because always incorporate the effect of eta later is not a big thing. You can just multiply it to the rate, okay, and I say adsorption and desorption; they are not really important or probably that we are doing at a very higher temperature, entire surface is available for reaction. Most of the sides are vacant; in that case, what I say is r is equal to, say, k. Now I am using k r; I will tell you why I am using k r here into c a. Again a first order reaction r a is equal to minus k r c a.

Now I want to bring these two effects together, okay. So, this is a reaction when this goes inside. So, that is why it is expressed for the concentration at a surface that is c a s. Why? C a s is going to be same everywhere, why? Because eta is one; so, whenever the reaction is taking place, it is at c a s concentration inside a particle. Now this c a s is not same as c a b and we are going to incorporate the effect of external mass transfer, okay. So, this is when the component reaches the external surface, okay.

Now what is the unit of this? This can have many units, okay. So, one unit would be that normally that we use it is per unit volume of the particle provided this is per unit volume. This can be per unit surface area provided by the particle, okay everywhere. Then in that case, this is per unit surface area, okay. This can be per unit weight of the catalyst. So, this would be per unit weight of the catalyst. Now we are defining one more unit; this is per unit area but not the internal area per unit external area external surface area; moles per meter square per second which is same as the unit is same as the external mass transfer, so that I can manage these two things, okay; they are in the same platform, alright.

So, this is this unit is moles per meter square per second. This is external surface area; do not confuse this area with the internal area s a that we have used before. So, this is s a but it has nothing do with this. This is the external area surface area which is for a spherical particle it is phi d p square, okay, alright. So, now this rate is expressed in the same unit as that of mass transfers flux, okay. That is why I am using k r here. So, k r is defined as the rate constant per unit external surface area; for that I need to know the shape of the catalyst; I am assuming it to be spherical here, okay, external surface area, so that I can now bring this same platform as that of the external mass transfer, okay.

Now at steady state, r is equal to or say as now r a is nothing but w a now because I am talking about a flux here per unit external surface area, okay, is equal to minus k r c a s and is equal to what? Minus k c c a surface minus c a b; oh, sorry it should be other way round; it should be b here and surface here. Both are negative negative; the magnitudes will be equal.

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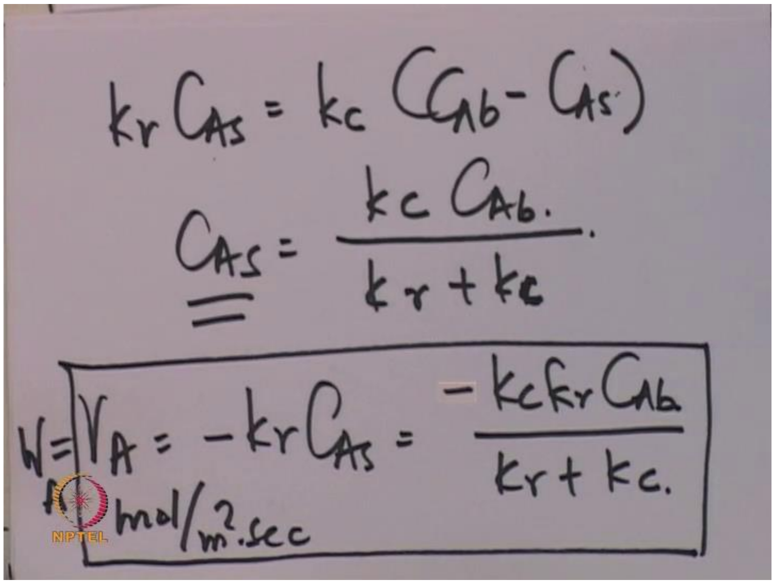

$$k_r C_{As} = k_c (C_{Ab} - C_{As})$$

$$\underline{\underline{C_{As}}} = \frac{k_c C_{Ab}.}{k_r + k_c}.$$

$$\boxed{W = r_A = -k_r C_{As} = \frac{-k_c k_r C_{Ab}}{k_r + k_c.} \quad \text{mol/m}^2\text{.sec}}$$

So, what I get here is k r c a s is equal to k c c a b minus c a s, look at this; these two are equal now, right. Now I get these; why they are equal? Because there is no accumulation at the external surface; see at a surface, surface is two dimensional, accumulation is zero, okay. So, whatever going to the surface is leaving the surface, okay; how much ever is going to the surface is same as there is no accumulation there. There is no source term at a surface; there is no sync term at the surface, okay. So, that is why the surface whatever is going external surface whatever is by mass transfer is getting reacted, okay. So, both are equal; that is the meaning of this.

Why we are equating now? Because mathematically we want to go further and get a simpler rate equation in terms of the external or bulk concentration, because it is the bulk concentration that I am got to deal with as far as the reactor design is concerned. Can I measure the surface concentration; can I sit on the external surface and measure it? No, I am aware of the bulk concentration only, okay. So, by rate equation the overall rate equation should be in terms of the bulk concentration; again the same logic.

What did we do for intraparticle case? There again the internal concentrations I did not know them or I cannot measure them rather; that is why I finally got expression for that in term of the external concentration and external surface. Similarly, for adsorption desorption, do I know the concentration I would have solved; I do not know the concentration. Do not know in the sense I cannot measure them, okay. So, I have just expressed them in terms of the bulk concentration, the same logic here, okay. So, at the external surface, I cannot measure concentration. And since I know that this external surface concentration is not same as the bulk concentration, I need to do this.

I need to express this external surface concentration in terms of bulk concentration, okay, alright. So, let us go ahead; from this, what I get is c a s is equal to k c c a b divided by k c plus k r, okay. So, I got the expression for c a s. Now I go ahead and substitute for c a s in the rate equation r a is equal to minus k r c a s is equal k c k r c a b divided by k r plus k c, and what is the unit here? Again do not forget moles per meter square per second and which is same as w a. So, this is my rate equation; this is my rate equation. Look at this rate question. This is again something similar to what we have got for adsorption desorption case; of course, the expression does not look similar, but the procedure is quite similar. That I laminated the concentration at the interface at the external surface, okay, and I have got this final expression which is in terms of bulk concentration, I am able to measure this.

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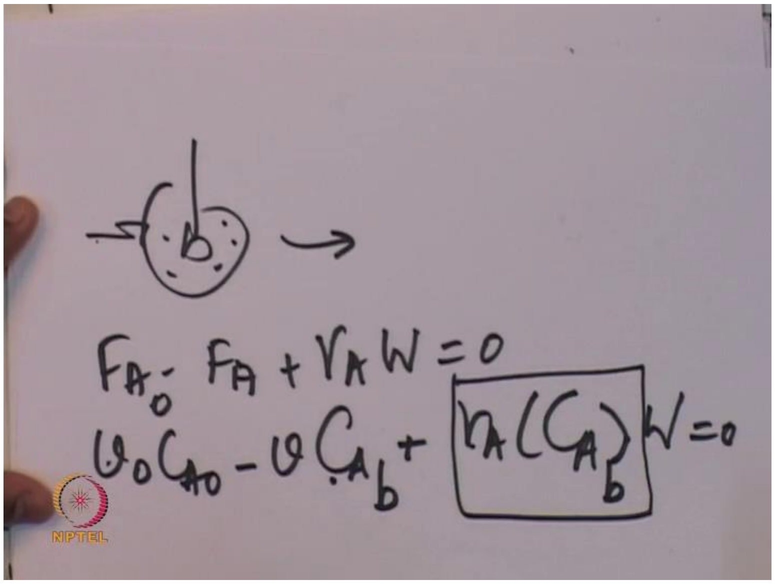

$$F_{A_0} - F_A + r_A W = 0$$

$$\upsilon_0 C_{A0} - \upsilon C_{A_b} + \boxed{r_A(C_{A_b})} W = 0$$

So, again similar to what we discussed before as well now if I have c s t r, I would design a c s t r, okay. I am dealing with the bulk concentration. So, f a 0 minus f a plus r a w is equal to zero. If I convert this into concentration, say and r a is again a function of concentrations. These concentrations are bulk concentrations, and that is why I need this expression r as a function of c a b and not c a s, okay, and that is why I have got this equation, okay. This equation I am going to use this equation in the design. Now look at this equation; there is so much that we can learn from this equation relative importance of k c and k r. The smaller one will govern the overall rate, okay, alright.

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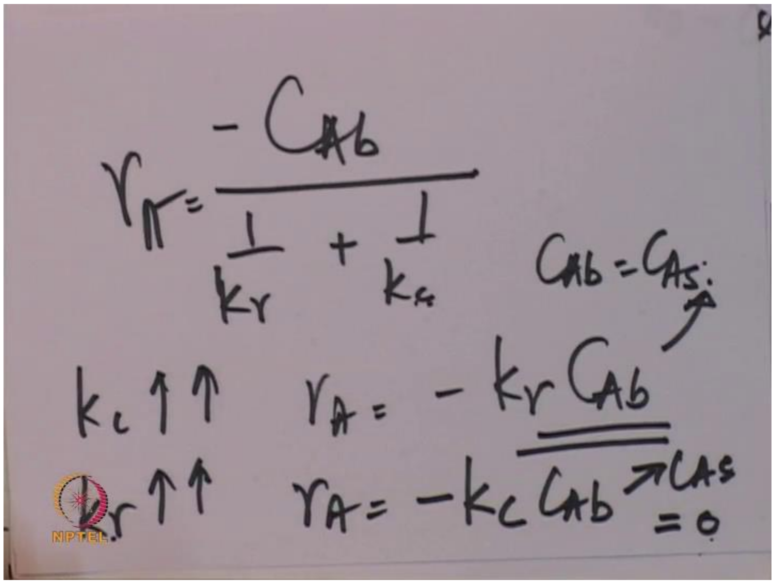

$$r_r = \frac{-C_{Ab}}{\frac{1}{k_r} + \frac{1}{k_c}}$$

$C_{Ab} = C_{As}$

$k_c \uparrow\uparrow \quad r_A = -\underline{\underline{k_r C_{Ab}}}$

$k_r \uparrow\uparrow \quad r_A = -k_c C_{Ab} \quad C_{As} = 0$

I can again convert it to this form r a is equal to c a b divided by 1 divided by k r 1 divided by k c same one. So, k c k r I have just taken in down. Now you can see if k c is very large, this becomes zero; sorry negative sign. Yeah, k c is very large; this becomes zero. So, it boils down to a normal kinetics, okay; for k c very large r a is equal to minus k r c a b intrinsic kinetic control; that means which is nothing but c a b is equal to c a s this situation, no external mass transfer resistance. K c is very large; diffusion resistance is negligible, mass transfer coefficient is very large. Either diffusivity is very large or delta is very small, okay.

Other way round, k r is very large no relatively, it is always relatively, large means what? Relative to k c, okay, k r is very large relative to k c, then r a is equal to minus k c c a b. In that case, what is c a s? C a s is almost negligible 0. Here c a s is equal to c a b whereas in this case, c a s is equal to zero; you can think about it, okay. We will continue this discussion in the next lecture, okay, but this is the meaning of the rate equation, okay. If k c is very large, then mass transfer resistance is negligible; I can ignore it, right. If k c is very small compared to k r, okay, right; in that case, I have to consider it, okay, that reaction becomes instantaneously. Our intrinsic reaction become instantaneous; the overall reaction is controlled or governed by the external mass transfer, okay. So, we will continue this discussion in next lecture.