Chemical Reaction Engineering II
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Lecture - 25
GLR-6: Reaction regimes in surface renewal theories (contd..)

Welcome back. We have been in the few lectures, looking at the effect of chemical reaction on mass transfer. And we first did this within the framework of the film theory and we found that the effect of the reaction can be studied, in order of increasing severity of reaction. And the various possibilities fall into several regimes. So, the reaction can be very slow relative to the mass transfer, in which case we have the slow reaction regime, in which the reaction takes place essentially within the bulk of the liquid. And the film has the role of simply conducting the solute, from the gas liquid interface to the bulk, where it reacts.

So, in that sense, the film and the bulk operate in series here. So, the film has diffusion and the bulk has reaction. And the diffusion and reaction operate in series. Now as often happens when rate processes take place in series, it is the slowest rate process that dictates the overall course of events. In other words, the overall driving force that is there; is partitioned in such a way, that the greatest share of the driving force is available to that process which has the highest specific resistance.

So, this, using this principle the a slow reaction regime gets further subdivided into a kinetic sub regime and a diffusional sub regime. The kinetic sub regime being 1 and which; the reaction is by far the much higher resistance as compared to the mass transfer. And in the diffusional sub regime, the diffusional resistance or the mass transfer step is the 1 which provides the greatest resistance and therefore, is the controlling resistance.

So, that is the slow reaction regime. And as the reactions becomes faster and faster, the occurrence of the reaction within the film, that is simultaneously with a diffusion can no longer be ignored and we have the transition to what we call as the fast reaction regime, which itself is a situation in which reaction and diffusion are taking place completely in parallel. There is nothing happening in the bulk, the bulk just acts as an inventory of the liquid phase reactant and serves to store the reaction product. But otherwise, everything that is of consent was; is actually happening within the diffusion film.

And as the reaction becomes faster and faster, the concentration profile of b starts to develop inside the diffusion film. In other words, variation in concentration of b within the diffusion film can no longer be neglected. And the reaction transits towards what is called as the instantaneous reaction. And the instantaneous reaction is an extreme situation, in which there is no region in the liquid which contains both a and b because, the 2 are so prone to react, that the moment a and b are present in the same place, they annihilate each other and produce the reaction product.

So; obviously, the reaction can take place only at a plane, to which, from the interface the mass transfer process supplies a and from the bulk the mass transfer process supplies b. And this supply of a and b is coordinated in such a way that, they arrive at the reaction plane, in the ratio in which they are required by the reaction Stoichiometry. And so this requirement fixes a position of the reaction plane and the position of the reaction plane in turn fixes the a magnitude of the enhancement factor that is possible. And this of course, is the maximum enhancement factor that is available to a system, given the concentrations of b and the concentration of a and so on.

So, this is the sequence of regimes that, reaction goes through, as the reaction velocity becomes higher and higher within the framework of the film theory. And in the last lecture, we started looking at the effect of reaction, within the framework of the surface renewal theories. And in order to keep the discussion simple and uniform, we decided to ignore the differences between the Higbie's version of the surface renewal theory and the Danckwerts version of the surface renewal theory; by defining a characteristic time tau which has 2 different connotations, slightly different connotations in the Higbie and the Danckwerts version of the surface renewal theories.

So, this characteristic time was used to non dimensionalize the time in the diffusion reaction equations. And we saw that, there is a place for something like this slow reaction, within the framework of the surface renewal theories as well because, it is a situation, in which once again the reaction is so slow that within the life time of the surface element, there is not too much reaction that occurs. And therefore, the concentration profiles develop just as if the reaction were not there.

So, of course, the physical mass transfer coefficient does not change because, it is governed by exactly the same equations as in the case of the physical mass transfer. And so we arrive at a situation where, the surface process is exactly the same as in the case of physical mass transfer. As a result of this surface process by the time, a surface element leaves the interface, it has a certain amount of a inside it. This a is delivered into the bulk where it now reacts.

So, in order to understand the effect of reaction, we go back to having to make a balance for the solute a within the liquid bulk. And of course, this works exactly the same way as a it does in the film theory because, what happens in the bulk is not subject to the film theory or the surface renewal theory, it is outside the ambit of both of these theories. It is a simple balance which says that, whatever is delivered by the mass transfer is consumed by the chemical reaction, if the bulk can be assume to be an a kind of quasi steady state.

So, everything that we said for slow reactions in the ambit of the film theory, applies verbatim to the case of the surface renewal theories. And therefore, we again can define a diffusional sub regime and a kinetic sub regime. Therefore, there is nothing different about the slow reaction regime, whether you talk about the slow reaction regime from a film theory its time point or from a surface renewal theory, its time point. Of course, we must remember in all this that, we are considering those reaction which can be while being second order, can be considered to be in a pseudo first order kind of situation because, the rate of supply of b to the places where the reaction occurs, is so much larger than the rate of which b needs to be supplied, in order to account for the reaction in proportion to in stoichiometry proportional to the rate of supply of a.

And therefore, the concentration of profile of concentration profile of b is essentially flat right upto the interface throughout the lifetime of the surface element. So, we will continue our discussions and to go situations, where the reaction is now of such a velocity that, it does make a difference to the diffusion process within the film.

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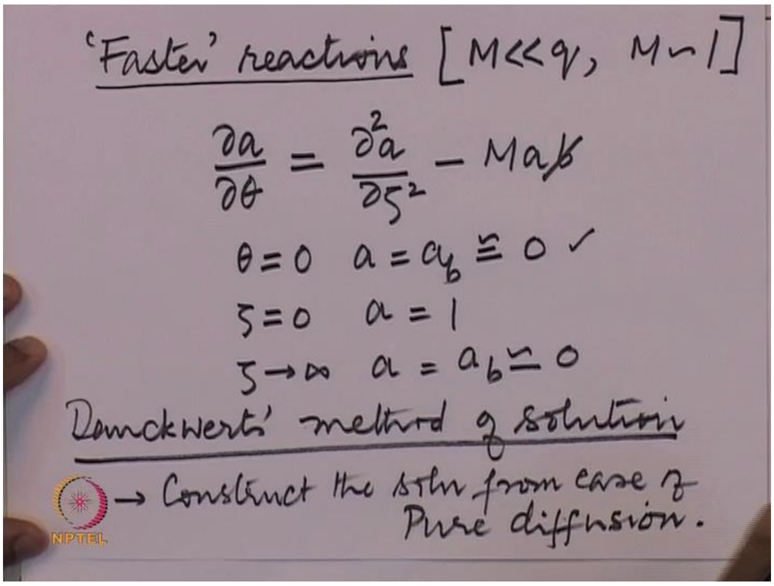

'Faster' reactions $[M << q, M \sim 1]$

$$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial \zeta^2} - Ma\cancel{b}$$

$\theta = 0 \quad a = a_b \cong 0$ ✓

$\zeta = 0 \quad a = 1$

$\zeta \to \infty \quad a = a_b \simeq 0$

Danckwerts' method of solution

→ Construct the soln from case of Pure diffusion.

In other words what we are saying is; we are looking at, let us say faster reactions. Faster in the sense of, these reactions do take place to an appreciable extent, within the lifetime of the element and therefore, they can no longer be ignored. So, the kind of situation we are considering is M far less than q, which ensures a pseudo first order regime. And M is of the order of 1.

So, under these situations, we have to solve in non dimensional terms. This equation we have written earlier. Of course, there is a b there which becomes equal to 1 and the relevant initial and boundary conditions are at theta equal to 0, a is a b and this is equal to 0 in most practical situations for reasons that we have elaborated earlier. And we shall make this assumption. We will not solve this equation for the general case of nonzero a b and for zeta equal to 0, a is 1 and as zeta tends to infinity a is a b which is once again 0.

Now, this is a much nastier equation than the equation that we solved in the case of film theory for a similar situation because, that was a steady state theory right. This is the partial differential equation, but there is a way of solving this; which was introduced by Danckwerts. And we shall simply indicate what this method is and leave the details to be worked out by you. So, this essentially constructs the solution from the case of pure diffusion.

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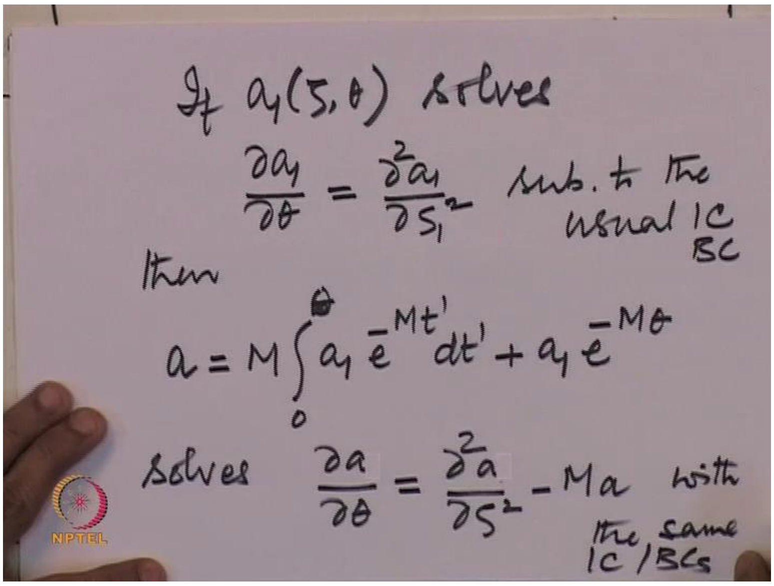

If $a_1(\zeta,\theta)$ solves

$$\frac{\partial a_1}{\partial \theta} = \frac{\partial^2 a_1}{\partial \zeta_1^2}$$ sub. to the usual IC BC

then

$$a = M\int_0^{\theta} a_1 e^{-Mt'} dt' + a_1 e^{-M\theta}$$

solves $$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial \zeta^2} - Ma$$ with the same IC / BCs

That is what Danckwerts says is that, if a 1 of zeta and theta solves, in other words if a 1 is a solution to the pure diffusion problem which is; d a 1 by d theta partial equals d squared a 1 by d zeta 1 squared. Then, so this is subject to the usual IC BC. Then, you can construct this quantity a in the following manner; M integral of integral from 0 to theta a 1 e to the power minus M t dash, where t dash is a dummy integration variable dt dash plus a 1 e to the power minus M theta.

So, this solves the diffusion reaction equation with the same IC and BC’s. So, in other words if you know the solution to this equation with, the initial and boundary initial boundary conditions that we have set out earlier, then we can construct the solution to the diffusion reaction equation by transforming the a 1 in this manner; the solution to the pure diffusion equation in that manner. The same initial and boundary conditions apply.

So, as we have seen the initial and boundary conditions do not change, whether there is reaction or there is no reaction. And we already know the solution of this 1, which is the pure diffusion equation. It is the error function complementary solution that we have written earlier. And therefore, we can use this method in order to calculate the solution of the diffusion reaction equation. So, when we do that. So, I will leave the details of that integration to you.

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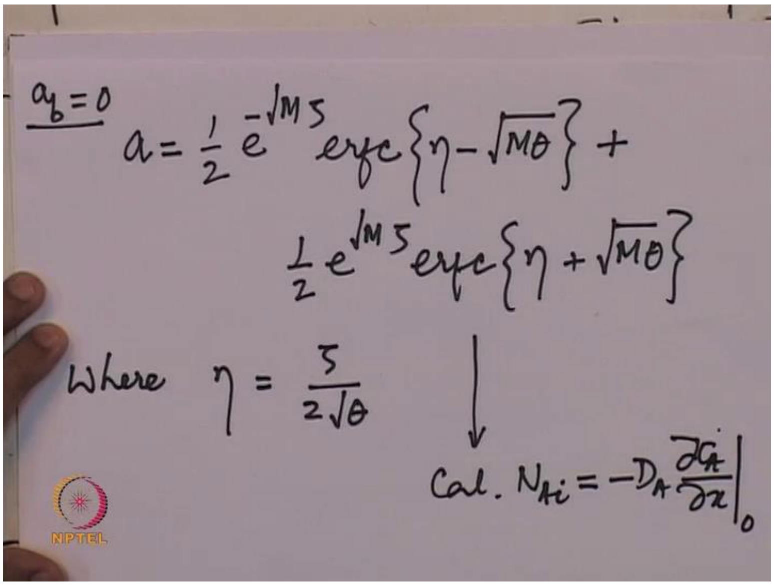

$\underline{a_b = 0}$

$$a = \frac{1}{2} e^{-\sqrt{M}\zeta} \operatorname{erfc}\left\{\eta - \sqrt{M\theta}\right\} + \frac{1}{2} e^{\sqrt{M}\zeta} \operatorname{erfc}\left\{\eta + \sqrt{M\theta}\right\}$$

Where $\eta = \frac{\zeta}{2\sqrt{\theta}}$

$\downarrow$

Cal. $N_{Ai} = -D_A \frac{\partial C_A}{\partial x}\Big|_0$

But the essential result is that, the concentration profile of a that is assuming that a b equal to 0, concentration profile of a is half e to the power minus square root of M zeta error function complement of eta minus square root of M theta plus half e to the power positive root M zeta error function complement eta plus square root of M theta, where this eta is the same combination variable that we have defined earlier and it is this quantity here. So, we know the concentration profile and from the concentration profile, we can calculate the instantaneous mass transfer flux as in non dimension, in dimensional terms it is D c A divided by dx equal to evaluated at x equal to 0.

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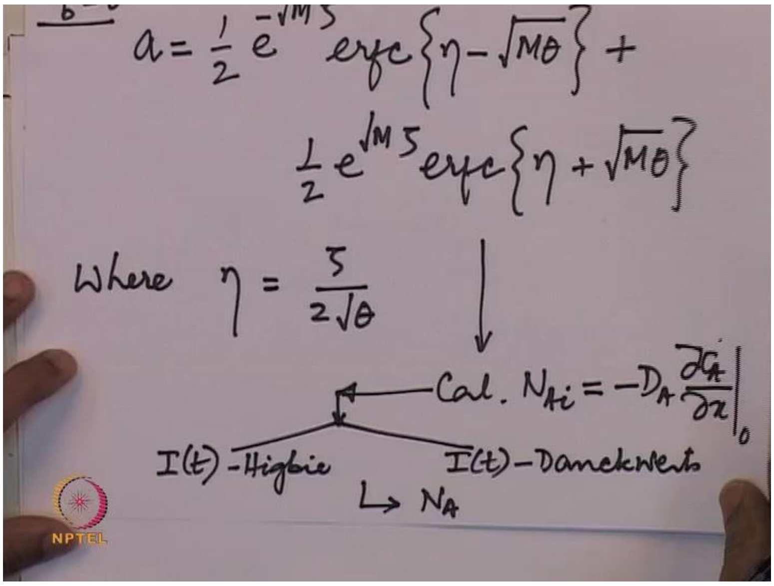

$$a = \frac{1}{2} e^{-\sqrt{M}\zeta} \operatorname{erfc}\left\{\eta - \sqrt{M\theta}\right\} + \frac{1}{2} e^{\sqrt{M}\zeta} \operatorname{erfc}\left\{\eta + \sqrt{M\theta}\right\}$$

Where $\eta = \frac{\zeta}{2\sqrt{\theta}}$

$\downarrow$

$\leftarrow$ Cal. $N_{Ai} = -D_A \frac{\partial C_A}{\partial x}\Big|_0$

$I(t)$ - Higbie

$I(t)$ - Danckwerts

$\hookrightarrow N_A$

So, we can do this and so once we do that, then we have 2 options. We can choose I of t for the Higbie or we can choose I of t for Danckwerts and we arrive at the average N A. So, this is the process.

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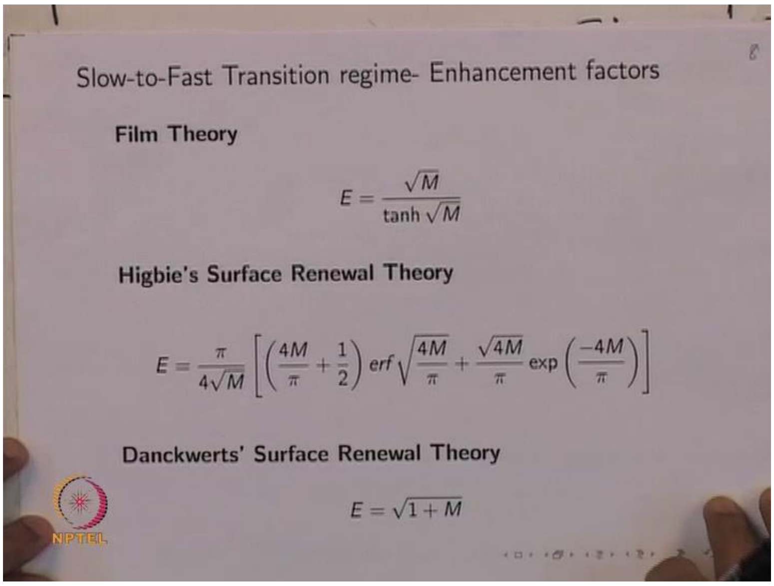

Slow-to-Fast Transition regime- Enhancement factors

Film Theory

$$E = \frac{\sqrt{M}}{\tanh\sqrt{M}}$$

Higbie's Surface Renewal Theory

$$E = \frac{\pi}{4\sqrt{M}}\left[\left(\frac{4M}{\pi}+\frac{1}{2}\right)erf\sqrt{\frac{4M}{\pi}}+\frac{\sqrt{4M}}{\pi}\exp\left(\frac{-4M}{\pi}\right)\right]$$

Danckwerts' Surface Renewal Theory

$$E = \sqrt{1+M}$$

So, if we did this, we arrive at an equation which is compared with the film theory equation in this slide here. So, we have already seen that the film theory gives you enhancement factor is equal to square root of M divided by tan h square root of M. If we did, if we go through the process that I described on the previous slide, then we and use the Higbie's i of t function in order to average out the instantaneous rates and compare that with the physical mass transfer rate. We find that the enhancement factor is given by this fairly complex expression, as compared to what we see here.

But on the other hand, the Danckwerts surface renewal theory gives a particularly simple expression for the enhancement factor, that is, square root of 1 plus square of the Hatta number 1 plus M. Now while these expressions look very different, it turns out that, if you actually put in the values of root M and calculate the numbers, they are not all that different.

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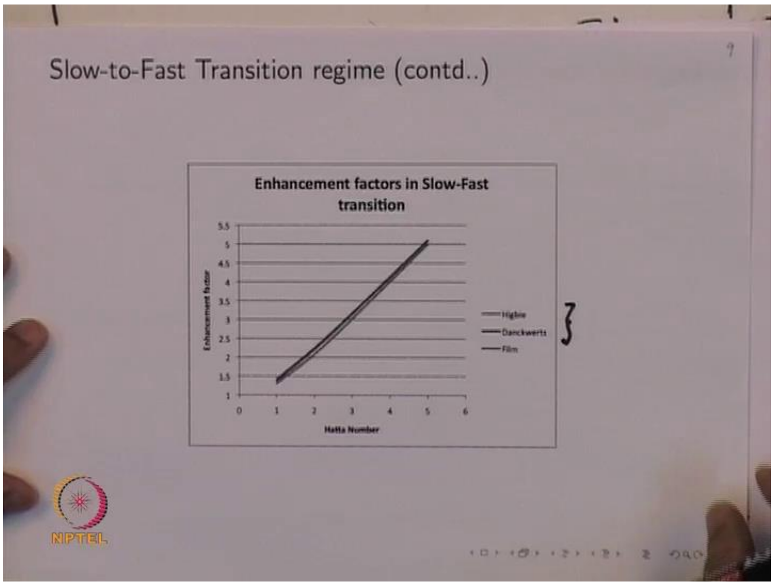

Slow-to-Fast Transition regime (contd..)

So, we illustrate that by making these calculations and comparing them for the slow to fast transition regime in this plot here, where the Hatta number is varied in the range of importance to us, that is, from root M equal to 1 to root M of about 5 or so and the enhancement factors are plotted and this scale goes from 1 to about 5.5. And we have the Higbie theory and the Danckwerts theory and the film theory compared here. And the Higbie and the Danckwerts theory, virtually fall on top of each other, there is that is the upper curve here and the lower curve is the film theory.

So, the film theory predicts slightly lower enhancements as compared to the surface renewal theory. And the surface renewal theory is pretty much agree in as far as the magnitude of the enhancement factor is concern. And the difference is actually very very small; it is a its about a few percent you know, it is about 7 to 8 percent at the maximum and you know at both ends the difference sustain to narrow out. And as you proceed in this direction, you are going to the a slow reaction regime.

Therefore, there the enhancement factor is 1 and as you go towards the higher reaches of this curve, that is as enhanced as Hatta number becomes faster and faster. Once again the curves approach each other. And there is a particular reason why the curves become more and more identical as enhancement factor increases. And as we know for as the Hatta number increases and as we know for Hatta number greater than 3, we have the fast reaction regime within the framework of the film theory.

We shall show in a moment; that the case of the surface renewal theories, also predicts the same kind of situation. And. In fact, it agrees identically in as far as its quantitative prediction of the enhancement for that situation is concern. But before we do that, let us try to understand from a point of view of a physical understanding, as to how the concentration profiles are developing in the case of the slow to fast regime transition. In other words, when our reaction is kind of fast enough to be taken into consideration while solving the processes in the surface element.

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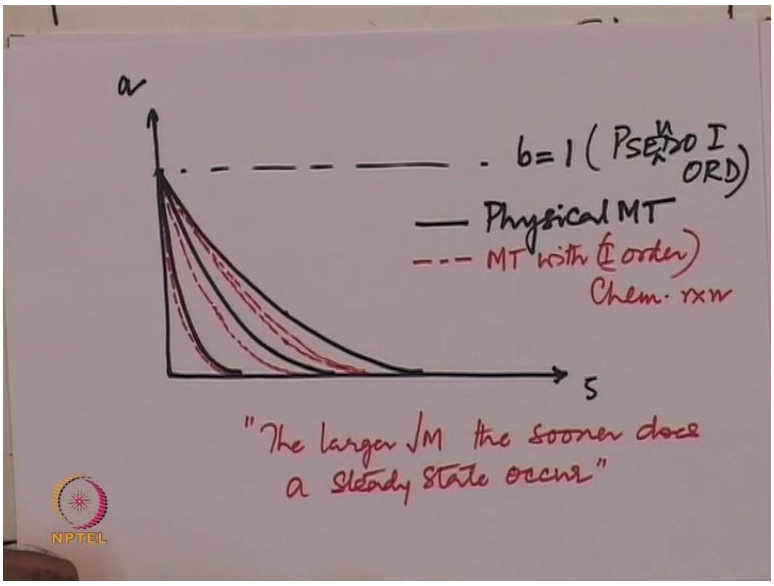

"The larger √M the sooner does a steady state occur"

So, let us look at those concentration profiles again. So, this is our zeta and this is our concentration profile of a. And the concentration profile of b throughout is 1. That is because; it is the pseudo first order. Now let us look at these concentration profiles. If you look at a short time, then the concentration profile of a will be something like this, at slightly longer times it will be like this, at even longer times it will be like this.

Now, let us look at what is the effect of chemical reaction. So, this is what I have drawn here; these black curves are physical mass transfer that is, there is no reaction taking place. Now what is the effect of chemical reaction? At every distance, at the same time, we would expect the concentration to be lower than in the case of physical mass transfer because, some of the a is being consumed by chemical reaction.

In other words, for this time, the concentration profile might look like this, for this time the concentration profile in the presence of chemical reaction, may look like this and for this time the concentration profile might look at this. So, what happens is; a longer the element spends at the surface, the greater is the difference between the red curve and the black curve. So, the red curve is the case of mass transfer with 1st order chemical reaction. So, there is another way of visualizing this situation.

So, what I just said was that, the longer the element spends at the interface, the greater is the difference at a given distance of the concentration it would have, as compare to the concentration it would have, in the case of physical mass transfer, because this is the cumulative effect. The longer it spends, greater is the amount that gets consumed. So, we can visualize this situation in another manner.

So, the mass transfer process is trying to push these concentration profiles, is getting to getting a to penetrate deeper and deeper into the surface element. On the other hand, reaction is trying to consume it and therefore, it tries to push it more and more towards the gas liquid interface itself. In other words, mass transfer tends to push the gas into the liquid, the reaction tends to consume it and prevent it from going further into the surface element.

So, the net result of these 2 processes which are at loggerheads with each other, you can imagine is that, the concentration profile does not proceed, does not get to proceed at the same rate, as it would in the case of physical mass transfer. In other words it lags behind. So, a limiting situation can be imagined in which; the tendency of the mass transfer to push the rate into the push the concentration profile into the surface element, is exactly balanced by the tendency of the reaction, to keep it from going forward at some stage. And therefore, the concentration profiles achieve some kind of a steady state.

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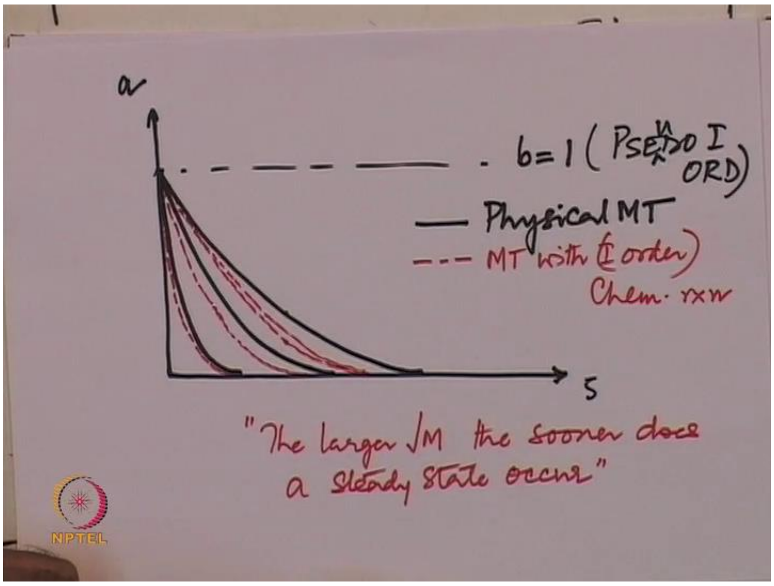

"The larger √M the sooner does a steady state occur"

In other words there are 2 opposing tendencies; 1 of which tends to get the gas to penetrate deeper into the system. The other of which tends to prevent this from happening. The 2 tendencies will operate at equal rates at some stage and at some point during the surface during the life of the surface element; the profile will stop from moving any further. In other words, so it will move like this and at a later time, it will not be much different from this and so on.

Now, the time at which this kind of a steady state occurs, depends on the value of the diffusion reaction parameter or the Hatta number. So, we can say the larger we can make the statement; the larger the value of root M, the sooner does a steady state occur. Now, this is a statement of some consequence because, you can imagine a situation in which the root M value is so large that, the steady state happens very early in the life of the surface element. If that happens, the surface element is going to spend a certain amount of time at the gas liquid interface; mucher the time is being spent in this steady state that we are talking about.

Therefore, in the; when it comes to averaging the local rate or the instantaneous rate with respect to time; you are essentially averaging a time independent instantaneous rate the steady state instantaneous rate.

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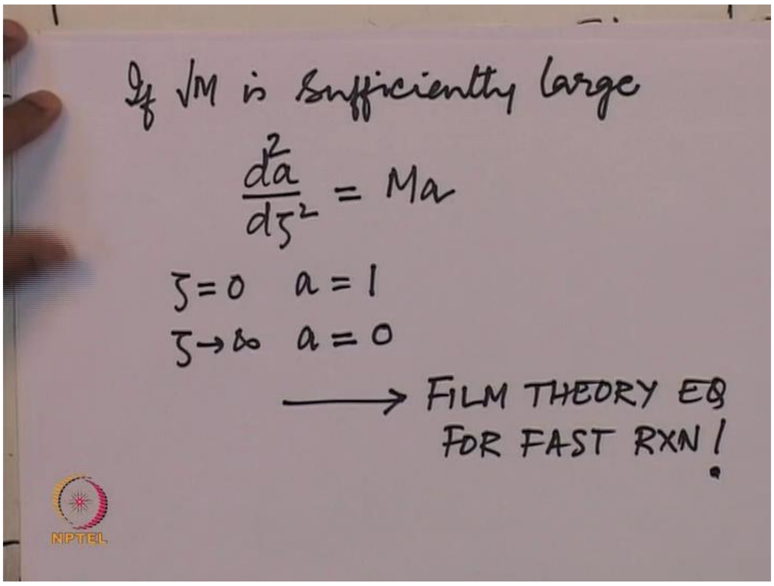

If $\sqrt{M}$ is sufficiently large

$$\frac{d^2a}{d\zeta^2} = Ma$$

$\zeta = 0 \quad a = 1$

$\zeta \to \infty \quad a = 0$

$\longrightarrow$ FILM THEORY EQ FOR FAST RXN!

So, if this is the situation that, if this is the limiting situation we are interested in, that situation is essentially governed by this equation. If root M is sufficiently large, then we can say that, we are essentially solving this equation, which is the steady state equation, with there is no initial condition required for this; 1 zeta equal to 0, a equal to 1 and zeta tending to infinity a equal to 0. Now if you look at this; this is exactly the same as the film theory equation for fast reaction. So, in order to just recollect that 1, we will just spend a minute, trying to see what the fast reaction was for the case of film theory.

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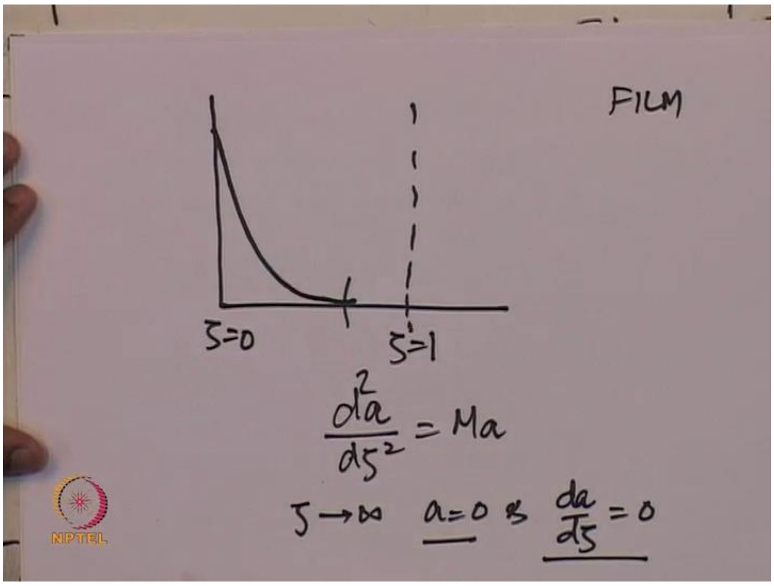

$$\frac{d^2a}{d\zeta^2} = Ma$$

$\zeta \to \infty \quad \underline{a = 0}$ & $\underline{\frac{da}{d\zeta} = 0}$

So, if you recall; this was the in the film theory. So, this was zeta equal to 1, that is, the end of the film, this is zeta equal to 0. And in general the concentration profile of a within the film theory, look something like this. And as far as this diffusing solute is concerned, because it is not going beyond a certain distance which lies within the film, the effective thickness of the film is infinite as far as the diffusing solute is concerned.

In other words, so this situation is; we had written the equation with the far boundary condition as zeta teeing to infinity, a equal to 0 and d a by d zeta equal to 0. The concentration and the flux both go to 0 as the distance increases. And for all practical purposes, the end of the film could be it does not matter if it is there or there or there because, the concentration profile does not know where the end of the film is.

So, we have an interesting situation that, we have these 2 theories; 1 is a steady state theory and it works in a finite field between x is equal to 0 and x is equal to delta. And then there is the other theory; the surface renewal variety of theories, which are unsteady state theories and they work in a semi infinite field. The diffusion occurs in a semi infinite field, bounded by the gas liquid interface at x is equal to 0, but really stretching to infinity on the other side.

Now, it turns out that, this is a situation the fast relation situation is 1 in which; the governing equations for the 2 theories become identical. So, this should not be surprising because for 2 reasons. 1 is if you recall, the resulting equations for the film theory treatment, we found that the results are independent of delta. That is because of course, what I said just a moment ago that, delta does not matter for the diffusing solute under these situations. Once it is independent of delta, which is a construct of the theory, the resulting equations are essentially independent of hydrodynamics. And hydrodynamics or the effect of hydrodynamics is the precise point, on which the film theory and the surface renewal theory have very different types of perceptions of the gas liquid mass transfer process.

Put another way what is happening here, is that, we have the film theory operating in the finite field, that is, between the diffusion takes place between x is equal to 0 and x is equal to delta. In the fast reactions regime, for all practical purposes, the x is equal to delta might as well lie at infinity. Therefore, the finiteness of the diffusion field does not matter, for the diffusion process. On the other hand, so in that respect, the film theory becomes something similar to the surface renewal theories, at least in so far as the mathematical formulation is concerned.

On the other hand, the surface renewal theory, which is an unsteady state theory, becomes essentially a steady state theory because, the fast reaction is such a situation, in which the reaction profile is arrested from proceeding in a time dependent manner into the liquid, very early in the life time of the surface element. And therefore, for substantial part of the life at the gas liquid interface, the gas liquid the surface element is absorbing the gas as if it were a steady state process.

So, it is a steady state process taking place in a semi infinite field as far as the surface renewal theory is concerned. It is a steady state process taking place in a semi infinite field as far as the film theory is concerned. So, the 2 processes become identical.

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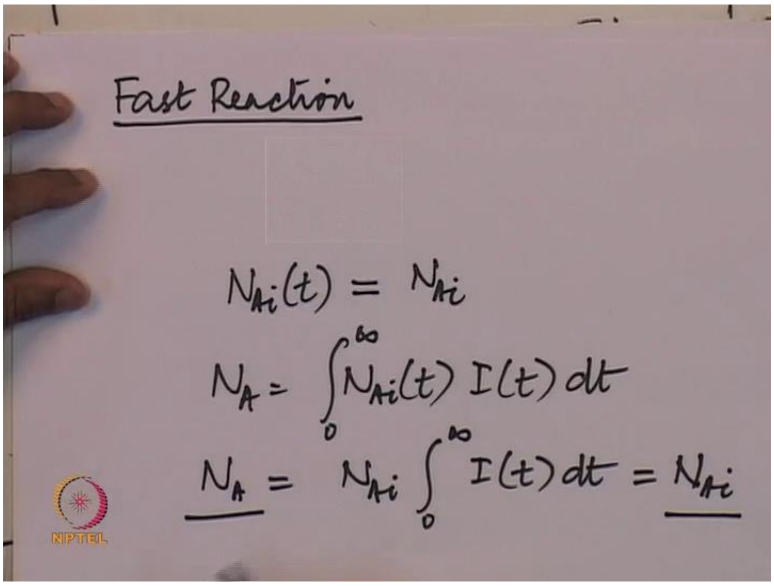

Fast Reaction

$$N_{Ai}(t) = N_{Ai}$$

$$N_A = \int_0^\infty N_{Ai}(t)\, I(t)\, dt$$

$$\underline{N_A} = N_{Ai}\int_0^\infty I(t)\, dt = \underline{N_{Ai}}$$

So, needless to say; since we are solving the same equations, we expect the same results. And so for fast reaction, so this is what is called as the fast reaction within the surface renewal theory. So, the definition of the fast reaction in the surface renewal theory is that, it is a situation in which the surface element essentially absorbs in a steady state manner, for a majority of it is a stay at the gas liquid interface. We expect no difference to be made by the choice of the i f t function because, whether it is surface renewal of the Higbie variety or surface renewal theory of the Danckwerts variety, we are averaging essentially a time independent function with respect to the; a waiting function and the waiting function itself is normalized.

Therefore, in other words, what I am saying is; if N A i of t is constant independent of N A i, then your average rate is N A i of t I of t dt 0 to infinity. This is N A i 0 to infinity I of t d t and this is nothing, but N A i itself. The average rate and the instantaneous rate agree, because it is a steady state process there is nothing to be averaged. So, we can now come back to the question that I raised very early in our consideration of the effect of chemical reactions on the mass transfer process. And I said that while the comparison of experimental data with the theories seems to suggest that, the film theory is less accurate, than the surface renewal theory in terms of the way it pictures the processes at the gas liquid interface.

We have seen in so far as the prediction of the effect of chemical reaction on the mass transfer coefficient. Or in other words, in so far as the prediction of the enhancement factor is concern, there is a slow reaction regime in which the 2 theories behave identically and there is a fast reaction regime in which once again the 2 theories behave identically.

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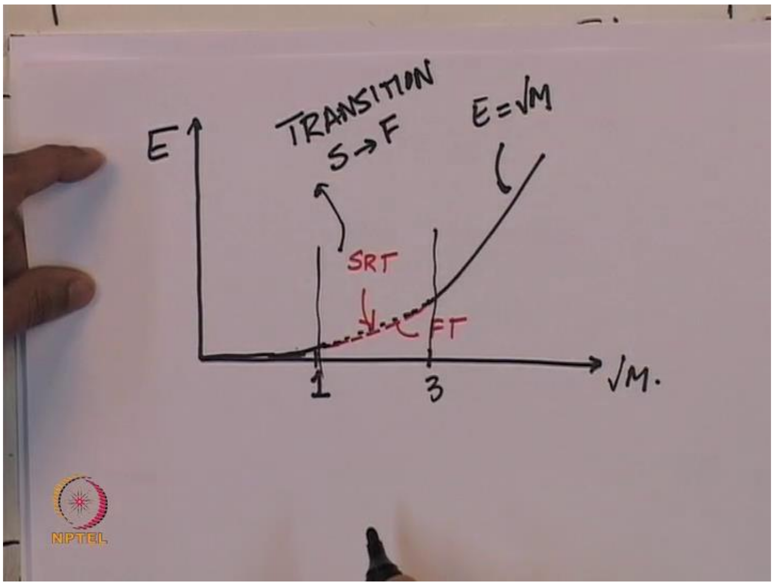

So, in order to picture this on the enhancement factor Hatta number diagram, we have a Hatta number of 1 and out here is the slow reaction regime and at round about 1, the curve starts to lift of and we have about 3. Incidentally, if you look at the way in which the equations work for the surface renewal theories, it is once again a value of 3 or 4 that around which, the equations become independent of time. The instantaneous absorption rate becomes essentially independent of time, very early in the surface elements edge. And therefore, the fast the precepts of the fast reaction regime, start applying from a value of about root M equal to 3.

So, that is clear from a numerical calculation; that becomes clear from a numerical calculation of the enhancement factor, from the transition regime equations. So, we have E equal to root M here. And from whatever we said earlier, we have the surface renewal theories there and the film theory here. In other words, this is the film theory and that is the surface renewal theory.

In other words, the theories are identical in this region and the theories are identical in that region, in between, you can always expect that, the theories are not going to be very different because, it is only a small region that we are considering.

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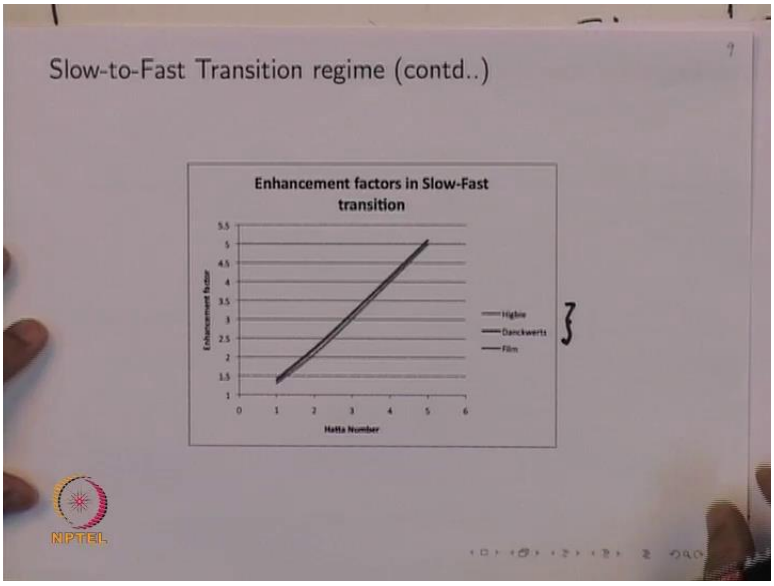

Slow-to-Fast Transition regime (contd..)

And given that, you are holding the 2 curves to definite asymptotes at the 2 ends, there is only so much they can do in between. And if you actually work out the numbers as we saw in this earlier curve, as we saw in this plot here, the difference between them is rather small.

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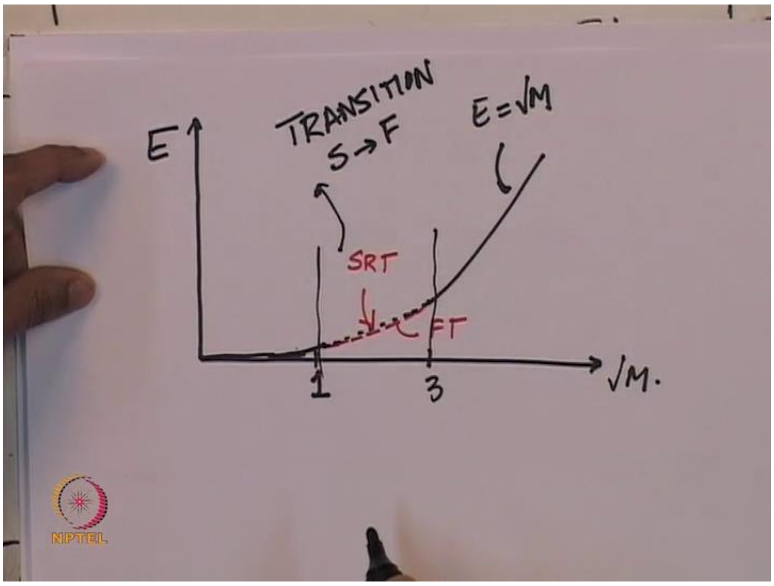

And therefore, we can continue to use either expression for the enhancement factor in the in this region in the so this region is the transition region transition slow to fast. So, then why do we need to … so we now take up the opposite question of so we were asking why are we looking at film theory at all, if film theory is not accurate. And we know surface renewal theories to be the better theories. And the answer is now clear that, the film theory gives the same results as the surface renewal theory, over a large part of the Hatta number range and we shall see what happens as we go to even larger hatta numbers in a moment. And it is a much simpler theory to conceptualize and solve. And therefore, we use the film theory.

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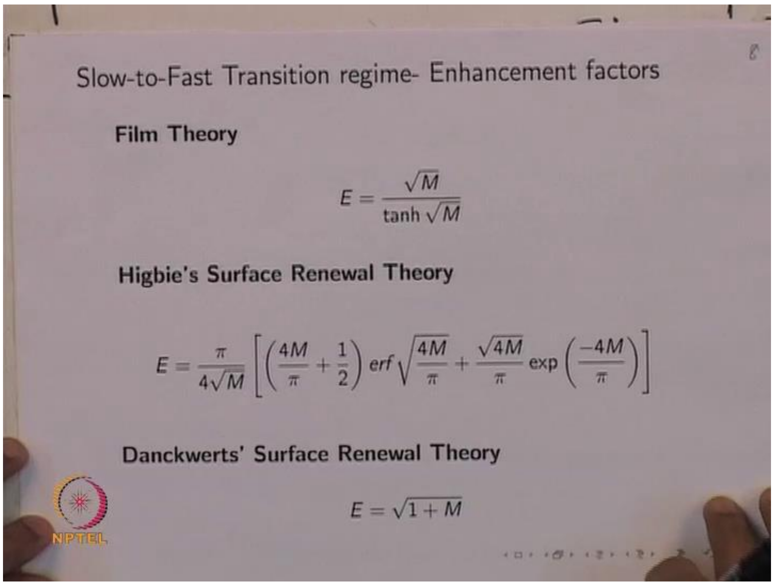

Slow-to-Fast Transition regime- Enhancement factors

Film Theory

$$E = \frac{\sqrt{M}}{\tanh\sqrt{M}}$$

Higbie's Surface Renewal Theory

$$E = \frac{\pi}{4\sqrt{M}}\left[\left(\frac{4M}{\pi}+\frac{1}{2}\right) erf\sqrt{\frac{4M}{\pi}} + \frac{\sqrt{4M}}{\pi}\exp\left(\frac{-4M}{\pi}\right)\right]$$

Danckwerts' Surface Renewal Theory

$$E = \sqrt{1+M}$$

So, the alternative question is; why do we then worry about the surface renewal theories at all at least in so far as what we have seen so far goes? The answer to that is; you have seen that the equations that result from the 3 theories are of different complexities. And this and the equations all look different. We go back to these 3 expressions that we showed. There is the film theory expression, there is the Higbie expression and there is the Danckwerts expression.

And this is sometimes of advantage because; you can use the equation that suits your purpose from the point of view of mathematical convenience, in order to design experiments and in order to calculate quantities of interest.

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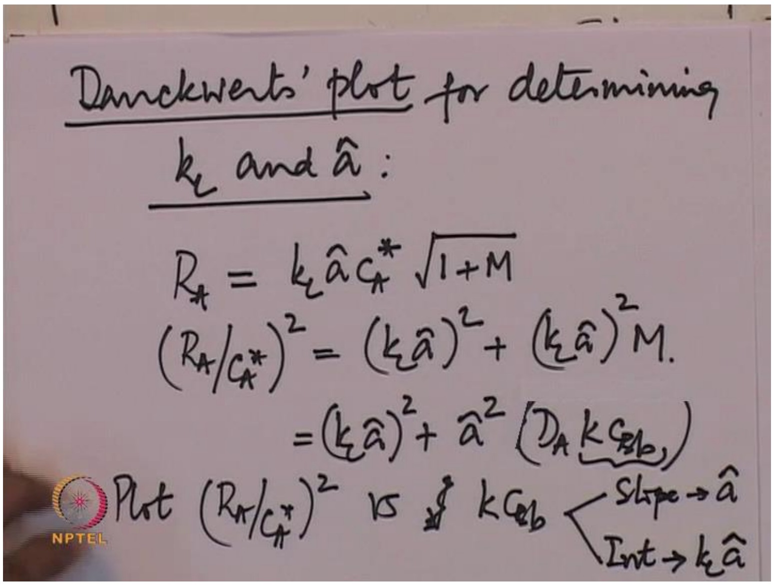

Danckwerts' plot for determining k_L and $\hat{a}$:

$$R_A = k_L \hat{a} C_A^* \sqrt{1+M}$$

$$(R_A/C_A^*)^2 = (k_L\hat{a})^2 + (k_L\hat{a})^2 M.$$

$$= (k_L\hat{a})^2 + \hat{a}^2 (D_A \underline{k C_{Bb}})$$

Plot $(R_A/C_A^*)^2$ vs $k C_{Bb}$ $\left\langle \begin{array}{l} \text{Slope} \rightarrow \hat{a} \\ \text{Int} \rightarrow k_L \hat{a} \end{array} \right.$

To take an example, the Danckwerts theory leads to the use of what is called as Danckwerts plot for determining k L and a separately. Now, this is usually a yet of ask because, you either have situations in which you can only determine k L a as a product or you can you have situations in which you can determine only interfacial area, that is, a fast reaction regime.

But, if you think about it, in the diffusional sub regime of the slow reaction regime, which is the 1 that that happens, before the reaction becomes fast enough to occur in the film, you have a rate that depends on k L a; the product of the mass transfer coefficient and the interfacial area. And on the other extreme, when it goes completely into the fast reaction, you have a rate that depends only on the interfacial range, that that does not depend on the mass transfer coefficient at all.

So, it stands to reason to expect that, in between that is, in the transition from slow to fast reaction regime, the rate of reaction should depend on k L a as a product as well as on the interfacial area. So, in other words both k L and a independently influence the rate in the transition regime. Now this is; while this can be anticipated, the expression that we use, that we have derived for this regime, is not very convenient to extract k L and a independently, if you consider the film theory expression or the higbie’s expression.

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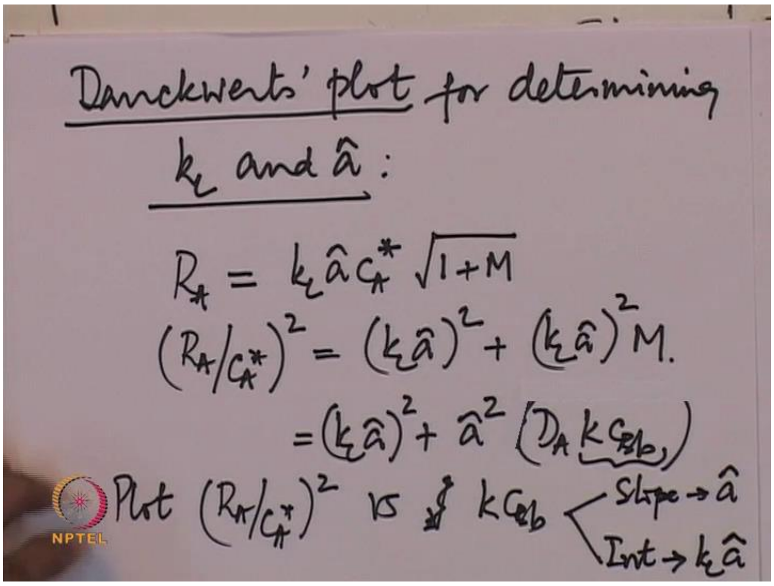

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Plot $(R_A/c_A^*)^2$ vs $k c_{Bb}$ $\begin{cases} \text{Slope} \rightarrow \hat{a} \\ \text{Int} \rightarrow k_L \hat{a} \end{cases}$

On the other hand, the Danckwerts expression allows you to do this. And that is the matter that I want to just spend a couple of minutes on. So, if you write the rate expression for Danckwerts theory, it is of course, k L a c A star multiplied by the enhancement factor which is in the Danckwerts theory 1 by M. So, if I take R A by c A and square it, then what I have is square of k L a plus square of k L a times M.

Now, so this is square of k L a plus a square, k L square will cancel with the k L squared in the denominator in M. And therefore, we are left with D A k c B b the pseudo first order rate constant. So, what this allows us to do is; if you can vary the pseudo first order rate constants; either by varying c B b or by making use of a catalyst in different amounts, which causes a variation in k itself and this is this is possible for very many reaction systems, then you can plot for different values of the pseudo first order rate constant, you can plot R A by c A star square versus k c B b.

If you do this, then you have a slope from which you can get interfacial area and you have an intercept from which you can get k L a. So, this is the advantage of the Danckwerts expression and given that, it gives you results which are numerically almost the same as any other theory. This can be used to advantage in the characterization of mass transfer equipment.

So, we shall leave the fast reaction regime behind at that point and look at the situation that arises when, the reactions that we are considering are even faster than what we have considered so far. So, the only assumption that has remained with us so far is the fact that the Hatta number is much less than q or M is less than much less than q. So, if this as M becomes larger and larger, as the relation becomes faster and faster, this assumption has to be violated at some point.

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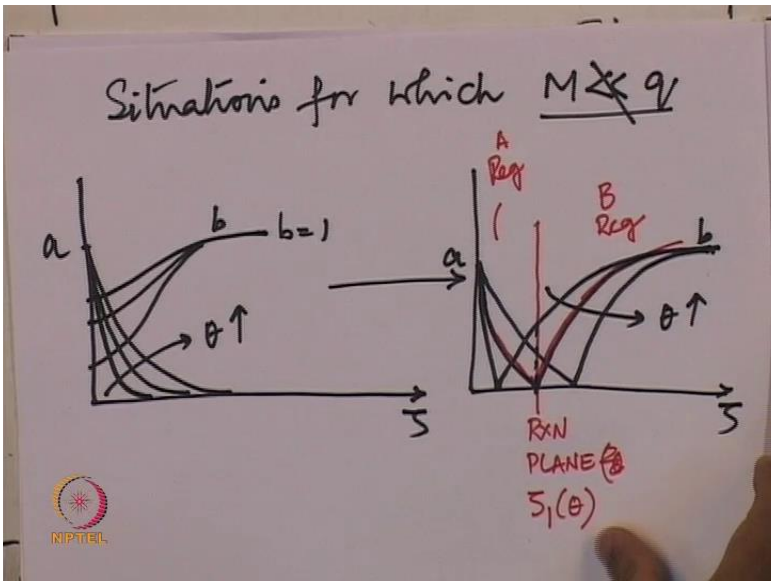

So, now we consider situations in which, situations for which, it is not true that M is far less than q. So, this assumption is violated. So, let us, it is clear that you know the equations have to be solved without any simplification at this for this case, in which by which what I mean is; you have got the second order partial differential equation for a, you have the second order partial differential equation for b. These are coupled because, the equation for a contains the concentration of b and the equation for b contains the concentration of a. There is a certain set of initial and boundary conditions.

So, this coupled set of non-linear partial differential equations, has to be solved for the case of M not much less than q. This is of course, not a easy task, it is not possible to do this by analytical means and you have to solve this by numerical techniques. But let us consider, physically what is happening much as we did in the case of the film theory, so that, we will see for are there any extreme situations that we can identify, in which we can derive a solutions for a much simpler set of equations.

So, we have these, you know we already are in the fast reaction regime and this is the concentration profile. And if this is the situation; if M is comparable to q then what happens is that, the concentration profile of q is no longer flat. I mean concentration profile for b is no longer flat and it decreases into the film. So, now, the unsteady state nature of the process comes into the 4 once again because, the concentration profile of a has developed to a an extent, but because of that b is consumed to a little extent near the interface. Because of which the reaction is slowed down, the concentration profile can push a little further; the concentration profile becomes deeper and so on.

So, as time goes on, you have situations of the profile developing in this manner. Now what happens is; at some stage during the life of the surface element, this concentration profile of b can hit the interface at b equal to 0. In other words, b is completely consumed at the interface. And later on what happens is that, there is a region that develops close to the interface which contains no b, much as we saw in the case of the film theory, except that in this case, the events are happening as a function of time within the same surface element. Now all this can happen pretty much pretty early in the life of a surface element if, M is much larger than q.

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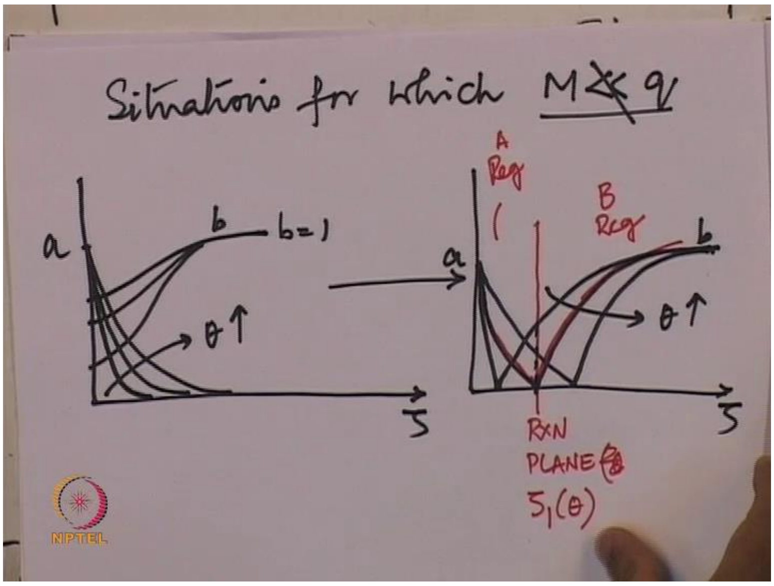

So, in that situation; so if we take an extreme situation, then what happens is; there is a region in which a is present, there is a region in which b is present, they do not overlap because, the reaction is so fast that, the 2 meet annihilate each other, consume each other at a plane. And this plane moves forward into the film as the surface element ages more and more. In other words, you may have a situation like this at short time and a situation like this at long times. So, this is zeta zeta. So, this is theta increasing and this is a and this is b right.

So, we have a situation in which, virtually throughout the life of the element. In other words, the surface element comes to the, the liquid element comes to the surface; at that instant the b at the interface is completely consumed. So, the concentration of b falls to 0 instantaneously the moment b reaches the interface. Because, there is no b now a can proceed a little into the film and so the point at which b come becomes 0 moves into the film. So, b is consumed at that point, now a can push a little further and so on. That is how you get this progression of profiles.

So, now what is the, if you take this central curve for example, let us look at this. Now this is a region which contains A, this is a region that contains B. And the 2 regions are separated by the reaction plane, which is not stationary as in the case of film theory. But the position reaction plane is at a position zeta 1, which changes with theta because; this is an unsteady state theory. So, the governing differential equations for this case look as follows.

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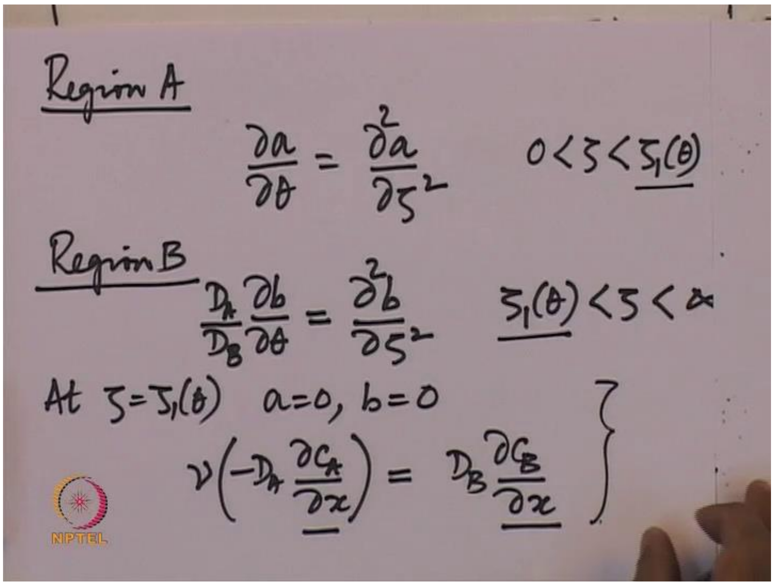

Region A

$$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial \zeta^2} \qquad 0<\zeta<\underline{\zeta_1(\theta)}$$

Region B

$$\frac{D_A}{D_B}\frac{\partial b}{\partial \theta} = \frac{\partial^2 b}{\partial \zeta^2} \qquad \underline{\zeta_1(\theta)}<\zeta<\infty$$

At $\zeta=\zeta_1(\theta)$ $a=0,\ b=0$

$$\left.\nu\left(-D_A \frac{\partial C_A}{\underline{\partial x}}\right) = D_B \frac{\partial C_B}{\underline{\partial x}}\right\}$$

In region A, we have d a upon d theta equals d squared a upon d zeta square, pure diffusion equation because, there is no reaction that can take place there, there is no b and. So, this applies between the interface and the reaction plane. In region B, so this region A only exists for time is greater than 0 and for region B you have a similar equation, except that you have ratio D A by D B and this applies between the reaction plane and infinity.

So, these are the 2 equations and the initial and boundary conditions work the same way except that, at the reaction plane at zeta equal to zeta 1 of theta, we have a equal to 0 and b equal to 0 and the fluxes have to be matched. So, the condition that determines, at what position the reaction occurs, is this condition that, nu times the flux of a equals the flux of b in the opposite direction. This is the same condition that we applied in the case of the film theory. But since now the partial derivatives of the concentration with respect to x are time dependent, this gives you a solution for zeta 1 that depends on time.

Now, this is what is known in Mathematics as a moving boundary problem, in the partial differential equation theory, as a moving boundary problem. And it is not easy to solve, but it can be solved analytically because, it is a much simpler equation, although it looks complicated, it is much simpler as compared to the situation in which you had the reaction term in both the equations and that brings about a nonlinearity.

So, these equations are linear. And if you look at the equations, you would suspect that, they would have error function type solutions. So, you can formulate an error function solution for this with 2 constants and error function solution for this with 2 additional constants. And these 4 constants have to be evaluated by the application of the initial and boundary conditions and this condition, this pair of conditions, which fixes the value of zeta 1 of theta.

So, this solution is of course, the mathematical details of this solution. We will not go through. It is available in books such as Danckwerts book on a gas liquid reactions and or even a bird Stewart light foot the book on transport phenomena. But what we will do when we come back is; we shall look at the final results of this solution what it leads to and what are the implications of that. And how those situations compare with the situation for … So, this is what we have formulated; is the case of the instantaneous reaction, within the framework of the surface renewal theories. So, we have the instantaneous reaction within the framework of the film theory. And we shall compare the results of these 2 theories, when we come back.