# Chemical Reactions Engineering II
## Prof. A. K .Suresh
## Department of Chemical Engineering
## Indian Institute of Technology, Bombay

## Lecture - 22
## GLR-3: Transition to fast reaction, and the Fast reaction regime

In the last lecture, we considered the effect of chemical reaction on mass transfer and considering that we are approaching the subject from the stand point of physical mass transfer in, which case there is no chemical reaction at all. It is logical that we start the consideration of chemical reactions from the slowest of them. And then, as we go along we consider reactions which are of increasing severalty that is faster and faster.

So, we started our consideration by considering the slow reactions. And we started this consideration within the frame work of film theory. Now, you do not have to be unduly perturbed at this stage that we are using film theory, which in the earlier lecture we said is, less realistic than the surface renewal theories. As we go long I hope to make it clear to you, that film theory does have a legitimate place in the a scheme of things, when it comes to predicting the effect of chemical reaction on mass transfer.

So, for the moment we will accept the film theory treatment and proceed. So, we set out the film theory equations. And we invoked a chemical reaction, which has the essential characteristics at we are looking for in other words, it has a dependence on the a the rate of the reaction has a dependence on the concentration of a, it has a dependence on the concentration of b.

But in order to keep matter simple we considered, a first order dependence which is about the simplest that we can think of. And also such a reaction that is a in the gas phase reacting with b which is the component of liquid phase. The stoichiometric being small nu moles of b being consume for every mole of a, to give a product remains in the liquid phase.

So, this is the kind of reaction that we are considering and in order to facilitate analysis we decided to approach the equations from a non dimensional perspective. And we choose a scheme of non dimensionalization which was such that, the non dimensionalized variables vary within the range of 0 to 1, and therefore they are of comparable magnitude.

So, when we did this it immediately became clear to us that when we talk about slow reactions and fast reactions and so on. We are not talking about the velocity of reaction in any absolute sense we are always talking about the velocity of reaction as it relates to the a velocity of diffusion.

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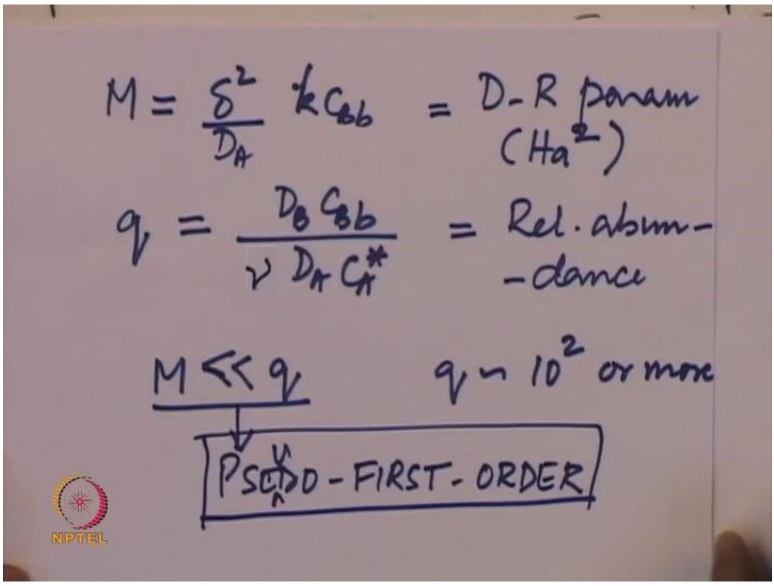

$M = \frac{\delta^2}{D_A} k C_{Bb}$ = D-R param ($Ha^2$)

$q = \frac{D_B C_{Bb}}{\nu D_A C_A^*}$ = Rel. abun-dance

$\underline{M << q}$ $q \sim 10^2$ or more

$\downarrow$

$\boxed{\text{PSEUDO-FIRST-ORDER}}$

So, we defined this dimensionless group which we called M which had this form and which is therefore, the ratio of the diffusion time scale to the reaction time scale. So, values of M which are very small would be identified as belonging to slow reactions; values of n which are large would be I mean would be taken to signify fast reactions. So, using this non dimensional group we wrote the reactions in non dimensional form.

And when we non dimensionalzed the equation for the concentration of b and other dimensional less group arrows which had this form and this we called as the relative abundance and this we can call as the diffusion reaction parameter. And it turns out to have a special name in the literature the square root of M is called as the Hatta number so; M would be called as square of the hatta number. So, with these 2 dimensionless groups we were able to write down the differential equations and the boundary conditions.

And then, we considered to start with those reactions for which, we do not have to worry about the dependence of the reaction rate on b. These happen to the those reaction where; the concentration of b is so large that the reaction is not able to make a significant dent in to the concentration. So in other words, the rate at which b is being supply to the into the film is so much larger than the rate at which it is required that the concentration of b remains virtually uniform write up to the gas liquid interface.

So, in quantitative terms this happens when M as a value that is much smaller than q and we make the point that q is usually of the order of 10 to the power 2 or more. There are systems for which q could be smaller, but it is usual to find q to be of this order of magnitude. And therefore, it is not unrealistic to imagine situations in which M is much less than q.

So, under these conditions the concentration profile of b is something that is flat that is that does not have to be bothered with and therefore, these qualified to be called as pseudo first order cases. So, this is the first thing that we started considering these pseudo first order case.

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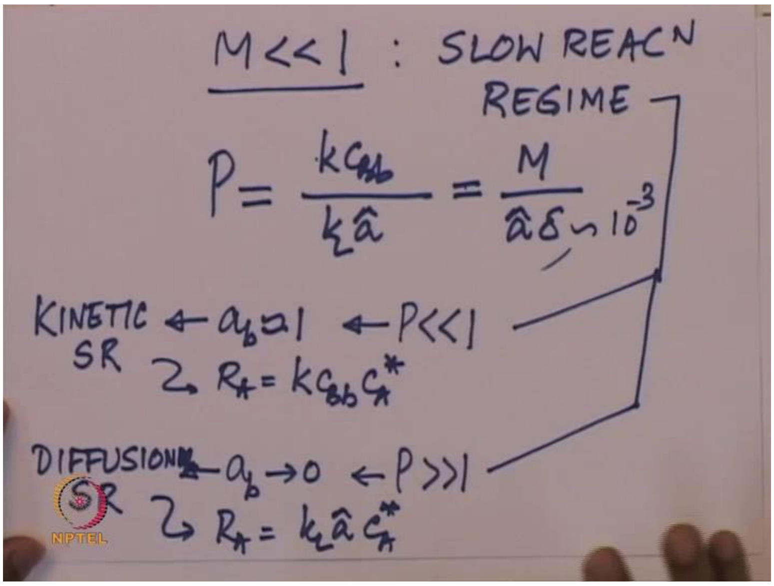

$\underline{M << 1}$ : SLOW REAC$^N$ REGIME

$$P = \frac{k c_{Bb}}{k_L \hat{a}} = \frac{M}{\hat{a}\delta} \quad \hat{a}\delta \sim 10^{-3}$$

KINETIC SR $\leftarrow a_b \simeq 1 \leftarrow P << 1$

$\Rightarrow R_A = k c_{Bb} c_A^*$

DIFFUSION SR $\leftarrow a_b \to 0 \leftarrow P >> 1$

$\Rightarrow R_A = k_L \hat{a} c_A^*$

And within that we made a further assumption that, the value of M is not only much less than q; it is much less than 1. So, these we can now call as belonging to the slow reaction regime and when this happens the reaction is so slow that it occurrence within the film can be completely neglected. The transport process within the film takes place just as if the reaction were not there.

So, the transport process delivers the certain flux of a into the bulk of the liquid and that is where the reaction exhausted influence. So, in order to see the effect of reaction it is pointless to look at the diffusion film itself. Because there the concentration profile remains linear as in the case of physical mass transfer; it is more useful to look at the bulk of the liquid that is the region of the liquid that is outside the film.

So, we made the point that this region is above 1000 times as large as the as the volume of liquid that is contain within the film itself. And therefore, even a small amount of reaction that takes place in this large volume is able to result in a significant consumption of a. So, this is the point that becomes relevant when we considered the what is called as the diffusional subregime. But so proceeding on this basis we made a balance for a in the liquid bulk; which we considered to be in kind of Quasi steady state.

In other words, any changes in concentration etcetera that are taking place in the bulk are taking place at a such a slow rate the mass transfer process can be a considered to be Quasi steady. Under these circumstances, can simply equate the flux of a that consign to the liquid bulk with the amount that is reacted within the bulk, by the chemical reaction which we take to be second order.

So, when we did this it turns out that the concentration of a within the bulk is set by the relative severity of the reaction relative to the mass transfer process. And we define another parameter P which was simply the reaction rate constant divided by the mass transfer rate constant if you like. So, this turns out to be equal to the ratio of M to this parameter a hat delta which is the ratio of the film volume to the bulk volume.

So, in terms P we can classify these slow reactions into, those reactions which are very, very slow for which M is so small. That in spite of being divided by a much smaller number a such as, hat delta which has the order of magnitude of 10 to the power minus 3 as we have demonstrated in spite of being divided by such a small number P still remains very, very small. That means that the rate of reaction is much smaller than the rate of mass transfer.

The mass transfer is able to pump the gas into the bulk till the bulk virtually becomes saturated. So, this leads to the concentration in the bulk being approximately equal to this saturation concentration or non dimensional terms the a b is equal to 1; the non dimensional concentration of bulk a concentration in the bulk of a is equal to 1. And this we called as the kinetic subregime.

On the other hand, it is possible given this small value of a hat delta that even for reasonably larger values of M the value of P can remain much greater than 1. In other words, we are saying that the multiplication by 10 to the power 3 in the numerator makes it possible for P to remain a greater than 1 even if M is considerably small. So, this under these conditions what we are saying is, that the reaction is much faster than the process of mass transfer here.

Therefore, ab tends to 0 negligible values and the reaction takes place in the bulk at very very small values of the concentration. So, this condition qualifies to be called as the diffusional subregime; in the kinetic subregime the rate of absorption would be given by the kinetic rate k cBb CA star, in the diffusional subregime the rate can be calculated as the mass transfer rate kL a CA star.

So, these are the points that we made it is important to realize the significance of the diffusional subregime. It arises only because of the fact that the ratio of the liquid in the film to the ratio volume of liquid in the bulk is very, very small. The bulk is about 1000 times larger than the film that is the only circumstance that leads to the occurrence of the diffusional subregime. And in the diffusional subregime all though we are saying that, the concentration of a in the bulk is very, very small that is not to say that there is no reaction occurring in the bulk.

Because, if you simply substitute this ab equal to 0 in the kinetic rate expression you will come up with the conclusion that, the rate of reaction is first order in a there is no a in the bulk. Therefore, there is no reaction in the bulk that is not the case because, we are saying that ab tends to 0 that is it has a values that is very, very small may be 10 percent, may be 5 percent, may be 1 percent of saturation.

But this small concentration of a is sufficient to cause a reasonable amount of a to b consumed in the bulk because of volume of liquid in the bulk is so large. So, the significance of diffusional subregime is a little difficult to grasp at first, but it deserved the attention. Because, it is adsorption important regime 1 which allows a calculation of certain mass transfer characteristics; before proceeding further to fast reactions let us try to fix these concepts by taking an example.

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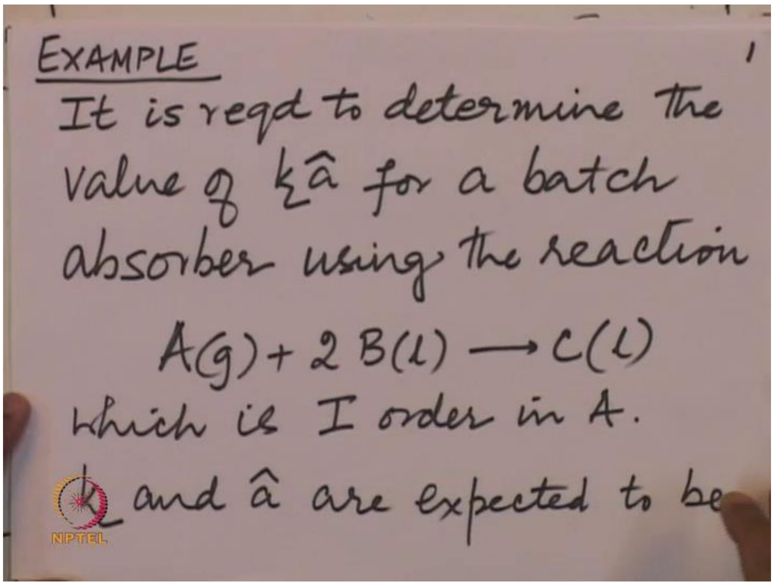

EXAMPLE

It is reqd to determine the value of $k_L\hat{a}$ for a batch absorber using the reaction

$$A(g) + 2B(l) \longrightarrow C(l)$$

which is I order in A.

$k_L$ and $\hat{a}$ are expected to be

So, this is the example that we wish to consider it is required to determine the value of the volumetric mass transfer coefficient or kL a for a batch absorber using the reaction A in the gas is reacting with 2 of B in the liquid phase gain C which remains in the liquid phase. So, this reaction is first order in A which means, to say that it has no dependence on the concentration of B; k L and a are expected to be of this order.

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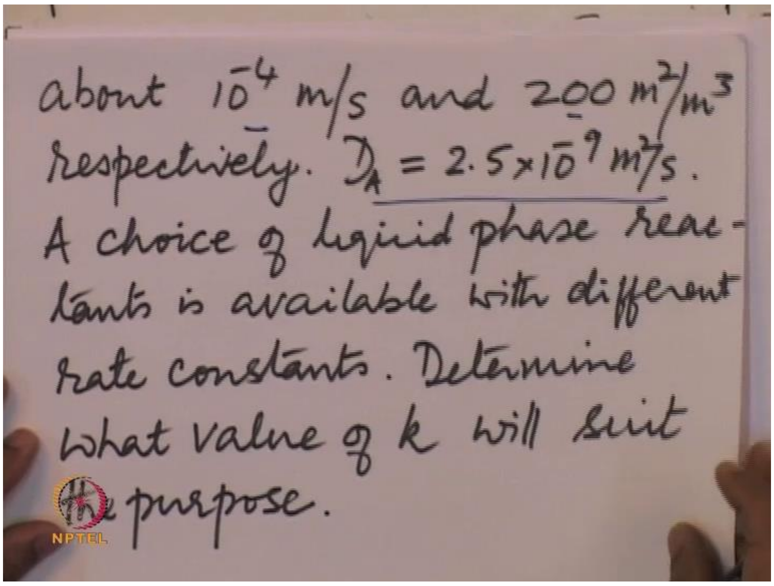

about $10^{-4}$ m/s and 200 $m^2/m^3$ respectively. $D_A = 2.5\times10^{-9}$ $m^2/s$. A choice of liquid phase reactants is available with different rate constants. Determine what value of k will suit the purpose.

So, we have a rough idea of the order of magnitude values of k L and a; k L is a expected to be about 10 to the power minus 4 meters per second in SI units and a hat that is the interfacial area per unit of volume of liquid is 200 square meters per meter cubed. The diffusivity of A in the liquid is given to be 2.5 into 10 raise to minus 9 square meters per second.

So, this is exactly known these are just order of magnitude estimates. A choice of liquid phase reactants is available with different rate constants. And you have to determine what value of k will suit the purpose. That is the purpose being the calculation of or the estimation of the volumetric mass transfer coefficient k L a. So, in order to estimate k L a how do we approach this problem?

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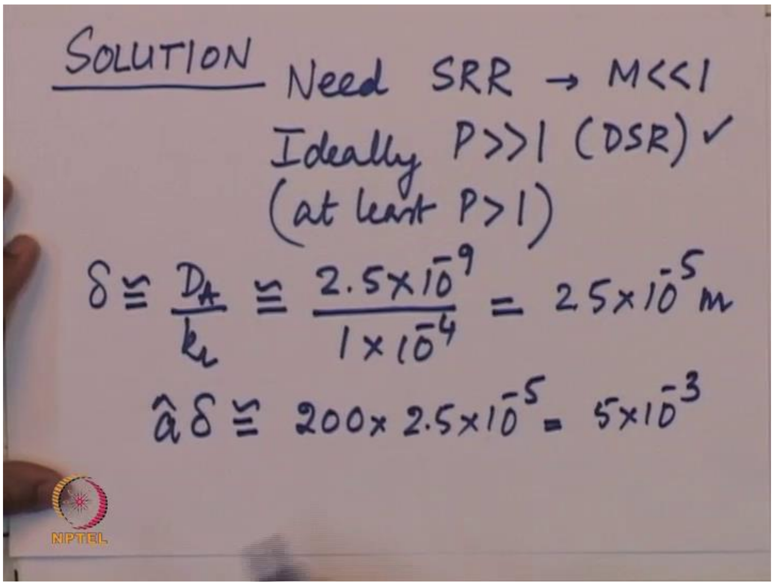

SOLUTION Need SRR → $M << 1$

Ideally $P >> 1$ (DSR) ✓

(at least $P > 1$)

$$\delta \cong \frac{D_A}{k_L} \cong \frac{2.5 \times 10^{-9}}{1 \times 10^{-4}} = 2.5 \times 10^{-5}\ m$$

$$\hat{a}\delta \cong 200 \times 2.5 \times 10^{-5} = 5 \times 10^{-3}$$

So, let us starts solving this problem so, in order to estimate k L a we need the slow reaction regime first of all. We may be I would a estimate k L a and others circumstances as we go long. But from whatever we know so far it is possible to estimate k L a under the flow reaction regime. So this means, first of all that we need a value of M; that is much less than 1.

Additionally, in the slow reaction regime if the value of p is very very small and the liquid become saturated. Then, the mass transfer has no role to play; the absorption rate is completely controlled by the kinetics. So, we do not want that kind of the situation. So, ideally we would also need P to be much greater than 1 that is the diffusional subregime or at least we need P greater than 1.

So that, the mass transfer has some significant role to play so, this is the best situation, where the rate of absorption if you measure is completely the rate of mass transfer and it is possible to uniquely calculate the rate of mass transfer. So, let us write down some expressions and let us calculate some numbers. First of all, we would like to estimate this delta the film thickness which is DA divided by k L and this is 2.5 into 10 raise to minus 9 divided by we do not have an exact value for k L.

In fact, the objective of the entire exercise to is to calculate k L a therefore, we can only calculate approximate values for these quantities and k L we have been told as a value of 1 into 10 raise to minus 4 meters per second. So, this gives you a value of 2.5 multiplied by 10 to the power minus 5 meters. So, given that a has a value of above 200, we can calculate the ratio of the film value to the bulk value.

And this turns out to be 5 multiplied by 10 to the power minus 3; that is 0.5 percent of the liquid that is present in the entire tank is water sides in the film. So, what is the value of M? So, this is this is sufficiently small we need to confirm this because, if this was large then, we should suspect that there is no diffusional of the subregime. So, we will not be able to estimate very accurately the value of k L a if this to be a small number.

In other words, if a hat delta was to be a small number then the purpose to be defatted. So, here we are all right because 5 into 10 raise to minus 3 sufficiently small and we suspect that there are reactions for which a diffusional of subregime is a very real possibility.

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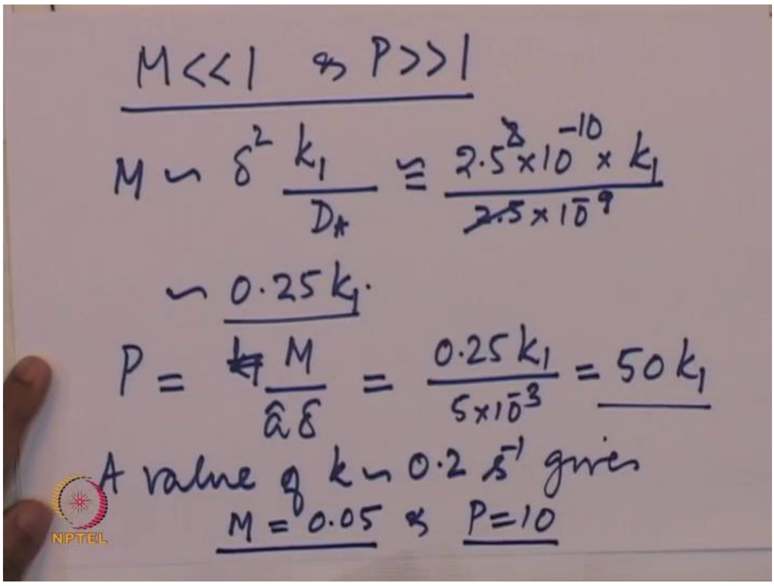

$$\underline{M << 1 \ \& \ P >> 1}$$

$$M \sim \delta^2 \frac{k_1}{D_A} \cong \frac{2.5^2 \times 10^{-10} \times k_1}{\cancel{2.5} \times 10^{-9}}$$

$$\sim \underline{0.25 k_1}.$$

$$P = \cancel{k_1} \frac{M}{\hat{a}\delta} = \frac{0.25 k_1}{5 \times 10^{-3}} = \underline{50 k_1}$$

A value of $k \sim 0.2 \ s^{-1}$ gives

$\underline{M = 0.05}$ & $\underline{P = 10}$

So, what are those kinds of reactions, those are reactions for which M is much less than 1 and P is much greater than 1. So, these are the kinds of reactions that we want. And M we can estimate once again, is delta squared in this case the first order rate constant itself given. So, that is k C Bb is replaced by the first order rate constant k1 divided by DA and so this is delta squared is 2.5 squared multiply by 10 to the power minus 10 k1 which is unknown. So, remember that these are again estimates divided by 2.5 multiplied by 10 to the power minus 9.

So, the 2.5 cancels and so, we are left with 10 to the power minus 1 from here. So, that is 2.5 k1 is the value of M. So, the value of k1 for example, if it has a value like 1 or 2 then M is 2.5 or 0.5 which is still much less than 1. What is P? P is nothing, but k1 or we can say M divided by a hat delta since we have calculated both of these quantities. And M is 0.25 k1 divided by a hat delta was 5 multiplied by 10 to the power minus 3. So, this gives you 50 k1.

So with these 2 numbers here we have to choose a value of k1 which keeps this small, but keeps this large. So, if you choose 2 a small value of k1 you will achieve this 1, but you may not achieve that 1. On the other, hand if you choose to larger value of k1, you will certainly achieve this 1, but this might be compromised. So we can try out a value of a case such has, A value of k which is like 0.2 second inverse gives M of 0.5 and P of 10. Now this is small enough, is this large enough that is the question.

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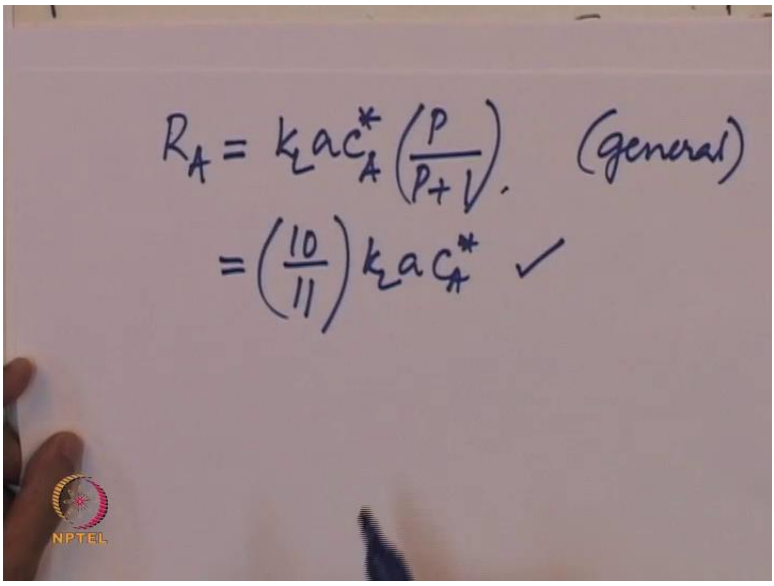

$$R_A = k_L a C_A^* \left(\frac{P}{P+1}\right). \quad \text{(general)}$$

$$= \left(\frac{10}{11}\right) k_L a C_A^* \checkmark$$

So, we can establish that by looking at the expression for the rate of mass transfer in the slow reaction regime in general. So, this is the general expression without assuming that the reaction is in the diffusional or the kinetic subregime. So, this if you recall from yesterday’s lecture is kL a CA star multiplied by P by P plus 1. Now, this factor P by P plus 1 is like 10 divided by 11 into kL a CA star. So, this is these are the factor that is close enough to 1 so, RA is approximately equal to kL a CA star.

Therefore, this is so we can get a reasonable estimate of kL a CA star. If you a reactant b for which the value of the rate constant is 0.2 second inverse. So what this simple example shows is that, the equations of slow reaction rate regime are useful in characterizing mass transfer equipment with respect to kL a; if a reactions of you know sufficiently slow rate constants are available.

On the other hand, you can sufficiently slow in the sense of it should be slow from the point of view of M it should be passed from point of view P. So, we have already established those conditions. So, the appropriate kind of reactions can be found. And this is often possible for example, if you take the example of absorption of Carbon dioxide into a solution of Amines; a choice of Amines available.

You can a choose Monoethanolamine, you can chose Diethylamine, you can use Triethanolamine and all of these have different rate of reaction. All for that matter you can chose any of a range of hinder amines for which again the rate constants are... So, it is always possible in a practical situation to find an appropriate reactant with right rate characteristics; that the mass transfer behavior of the vessel in terms of the volumetric mass transfer coefficient k L a can be completely characterized.

On the other hand, you can chose a reaction that is very, very slow and use the measured absorption rate to accurately calculate the value of the rate constant itself. So, this is a situation that is not unlike homogeneous reactions, if the reaction is very, very slow that is to say M is much less than 1 and also P is much less than under those conditions; you are in the kinetic subregime.

The reaction rate is given by the absorption rate is given by the reaction rate expression with the maximum values of the concentration of b and the concentration of a substituted; both of which are known to start with and in a batch process you can conduct batch runs. And interpret them as you did interpret homogeneous reaction and work out all the characteristics of the reaction rate expression.

So, these are 2 things that can be done using these expressions from an experimental point of view; from a point of view of a fundamental a study of reaction and mass transfer parameters. On the other side, if you want to design a reactor and the mass transfer behavior of that kind of reactor has been characterized earlier you have an idea of what the k L a is and the reaction is being well studied.

So, you know what the rate behavior is then, you can work out these numbers. And determine whether the reaction is in the slow reaction regime and if it is in the slow reaction regime, you can an appropriate expression of this type of this type here and use that to a design the reactor.

So, a we have a what we have said is, that a we have sufficiently understood the slow reaction regime in the sense that we can now use our understanding to number 1 interpret the rate parameters whether it is kL a or whether it is the reaction rate constant. And on the other hand we can also use our understanding through to design reactors for situations, where the reaction happens to be in the slow reaction regime.

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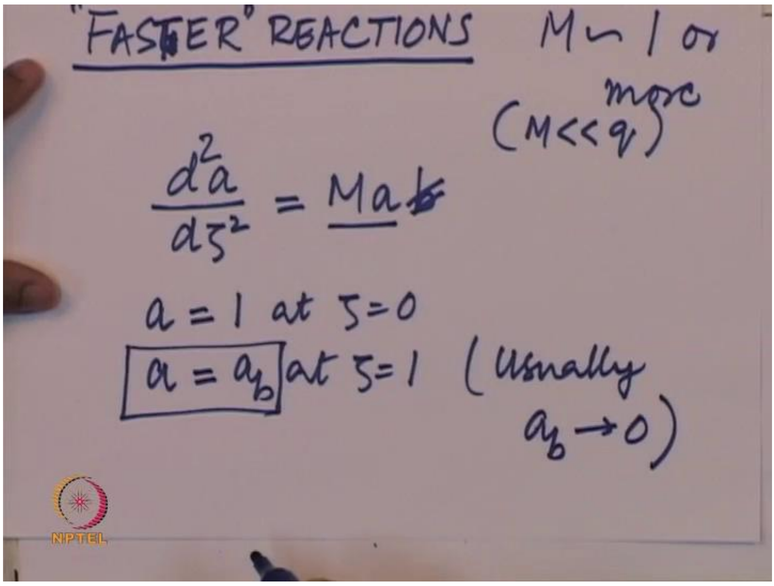

"FASTER" REACTIONS

$M \sim 1$ or more $(M << q)$

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

$a = 1$ at $\zeta = 0$

$\boxed{a = a_b}$ at $\zeta = 1$ (Usually $a_b \rightarrow 0$)

.

So, let us proceed further on that bases and now we will consider, Faster Reactions I put faster within united comma we will give more descriptive names to the kind of regimes that we are considering as we go long. But this is faster in the sense that, now we are considering values of M which are not necessarily much smaller than 1 they are about 1 or more. But it remains a fact that M is far less than q so these pseudo first order assumption is still valid.

So, we recall this equation that we wrote yesterday and because, we have a pseudo first order regime we do not have to consider b. So, we have got a what for all practical purposes first order reaction in non dimensional terms. And the boundary conditions are a is equal to 1 at zeta equal to 0 and a equals a b at zeta equal to 1. A brief comment about this boundary condition here for all practical purposes, when write this non 0 term on the right hand side the reaction is already fast enough that ab is nearly 0.

That is because, even 1 this was 0 even when the value of M was so small that we did not have to consider it on the right hand side of this equation. If we vary the value of the reaction rate constant, we come to the diffusional subregime where already ab is tending to 0. So, even under those circumstances M is much smaller than 1. Therefore, when we come to 1 we are already pass the situation where the reaction needs to be fast enough to keep the concentration of a in the bulk at 0.

Therefore, ab can usually be replaced by 0, but for the moment we will solve it for general values of ab and we will invoke this assumption at the appropriate time. So, if you look at this equation it is a sufficiently innocent looking ordinary differential equation of the first order. And you know that these kinds of equations have solutions of the form e to the power P zeta.

And the value of P what are called as Eigen values are obtained by substituting this in this equations and deriving what is called as a characteristic equation. So, for this case if you substitute here you will get p squared e to the power p zeta here, M times e to the power p zeta here and canceling out e to the power p zeta from both sides.

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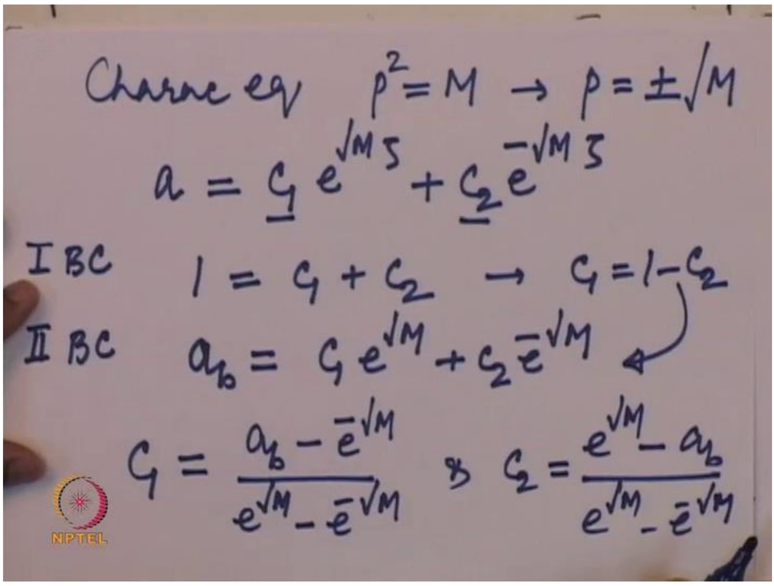

Charac eq $p^2 = M \rightarrow p = \pm\sqrt{M}$

$$a = \underline{c_1}\, e^{\sqrt{M}\zeta} + \underline{c_2}\, e^{-\sqrt{M}\zeta}$$

I BC $1 = c_1 + c_2 \rightarrow c_1 = 1 - c_2$

II BC $a_b = c_1 e^{\sqrt{M}} + c_2 e^{-\sqrt{M}}$

$$c_1 = \frac{a_b - e^{-\sqrt{M}}}{e^{\sqrt{M}} - e^{-\sqrt{M}}} \quad \& \quad c_2 = \frac{e^{\sqrt{M}} - a_b}{e^{\sqrt{M}} - e^{-\sqrt{M}}}$$

.

We get the characteristic equation as follows is P squared equals M and which means, P can take 2 values plus or minus square root of M. Therefore, the general solution invoking the principal of super position for linear systems can be written as a equals c1 1 integration constant e to the power root m zeta plus c2 a second integration constant, e to the power minus root m zeta.

So, we need to calculate the values of these 2 constants c1 and c2 by invoking the boundary conditions. And if we invoke the first boundary condition which says that, at the zeta equal to 0 a has a value of 1 we have 1 equals c1 plus zeta c2 zeta equal to 0 makes this term 1, zeta equal to 0 makes that term 1 as well. And if you invoke so this means, that 1 of the constants can be represented in terms of the other and if we invoke the second boundary condition, we have ab is equal to c1 e to the power root M plus c2 e to the power minus root M.

So, we can substitute this into this and find out a value of c2 and resubstitute back that in that and find out a value of c1. And I will leave to you to do those algebraic manipulations and give you the final equations for the 2 constants c1 is that c2 is e to the power root M minus ab divided by e to the power root M minus e to the power minus root M. You will recall the definition of hyperbolic trigonometric functions and realize that these quantities can write in terms of hyperbolic signs. But we will do that in a minute if we substitute these values of c1 and c2 in to this expression here.

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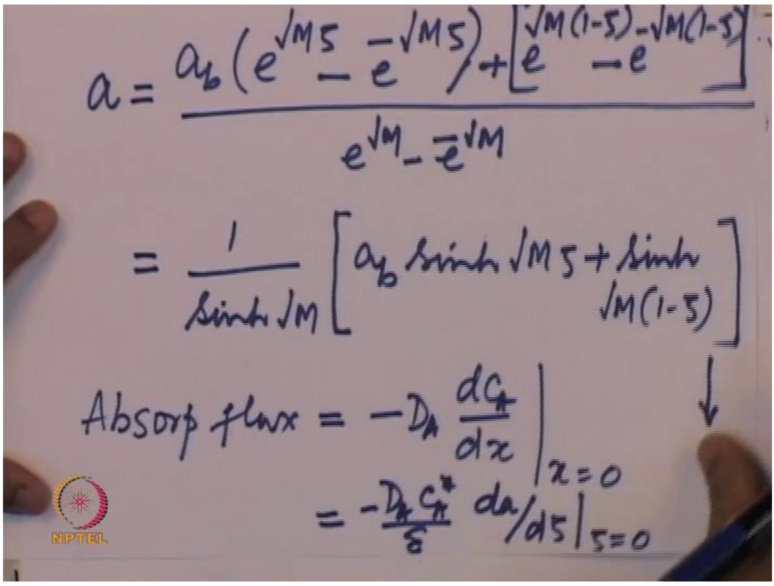

$$a = \frac{a_b\left(e^{\sqrt{M}\zeta} - e^{-\sqrt{M}\zeta}\right) + \left[e^{\sqrt{M}(1-\zeta)} - e^{-\sqrt{M}(1-\zeta)}\right]}{e^{\sqrt{M}} - e^{-\sqrt{M}}}$$

$$= \frac{1}{\sinh\sqrt{M}}\left[a_b \sinh\sqrt{M}\zeta + \sinh\sqrt{M}(1-\zeta)\right]$$

$$\text{Absorp flux} = -D_A \frac{dC_A}{dx}\Big|_{x=0} \downarrow$$

$$= -\frac{D_A C_A^*}{\delta} \, da/d\zeta\Big|_{\zeta=0}$$

We get the final expression for the concentration of a which is ab e to the power square root of M zeta minus e to the power minus square root of M zeta plus e to the power root M 1 minus zeta minus e to the power minus root M 1 minus zeta divided by e to the power root M minus e to the power minus root M. So, as I mentioned a moment ago writing in terms of hyperbolic sins. And cosines and so on this can be written as 1 by sin h root M ab sin h root M zeta plus sin h root M 1 minus zeta.

So, this is the a concentration profile and what we are interested is of course, the absorption flux and this is nothing, but minus DA d CA dx at x equal to 0. Or in terms of the dimensional less numbers that we are working with it is DA CA star divided by delta d a divided by d zeta evaluated at zeta equal to 0, which means we have to differentiate this with respect to zeta and evaluate the derivative at zeta equal to 0 substitute in to this in order to get the absorption flux.

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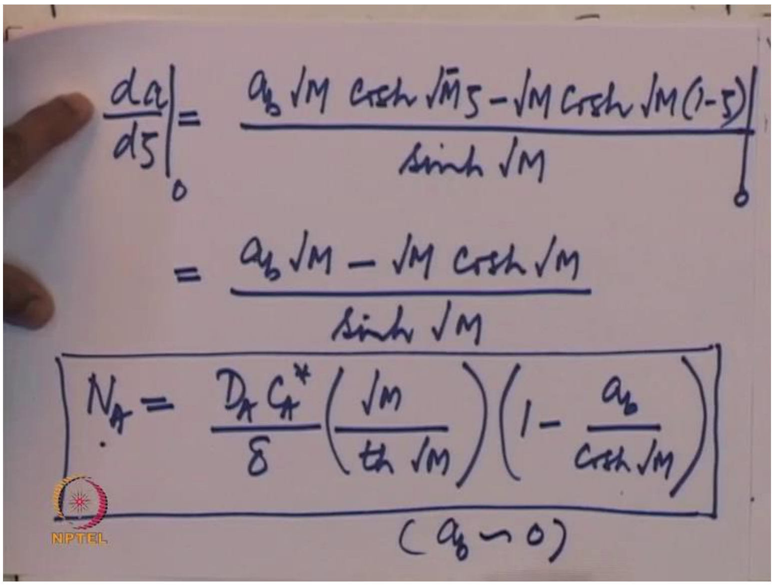

$$\left.\frac{da}{d\zeta}\right|_0 = \left.\frac{a_b\sqrt{M}\cosh\sqrt{M}\zeta - \sqrt{M}\cosh\sqrt{M}(1-\zeta)}{\sinh\sqrt{M}}\right|_0$$

$$= \frac{a_b\sqrt{M} - \sqrt{M}\cosh\sqrt{M}}{\sinh\sqrt{M}}$$

$$\boxed{N_A = \frac{D_A C_A^*}{\delta}\left(\frac{\sqrt{M}}{\text{th}\sqrt{M}}\right)\left(1 - \frac{a_b}{\cosh\sqrt{M}}\right)}$$

$$(a_b \sim 0)$$

So, da by d zeta if you differentiate it is clearly ab root M cosh root M zeta minus root M cosh root M 1 minus zeta divided by sinh of root M. So, this at if I want to evaluate at this 0 evaluate that at 0 then, this gives me a b root M. Because, cosh of 0 is 1 minus root M cosh of root M divided by sinh of root M.

So, if you substitute this in the expression for NA we get the following expression DA CA star divided by delta root M divided by tanh root M 1 minus ab divided by cosh root

M. This equation makes an important point what it says is, that NA under these circumstances is not linear in the concentration driving force CA star minus C ab.

Because, you know it should have been 1 minus ab to give a linear driving force because of the presence of this cosh root M here, it is not simply the CA star minus cb that drives the absorption flux under these conditions. However, so this makes it little difficult to compare this with physical mass transfer situation, where the driving force is given by CA star minus C ab. However, the saving grace is because of the small value of a hat delta because of which we recall that ab usually is of the order of 0 by the time we start to use expressions of this kind.

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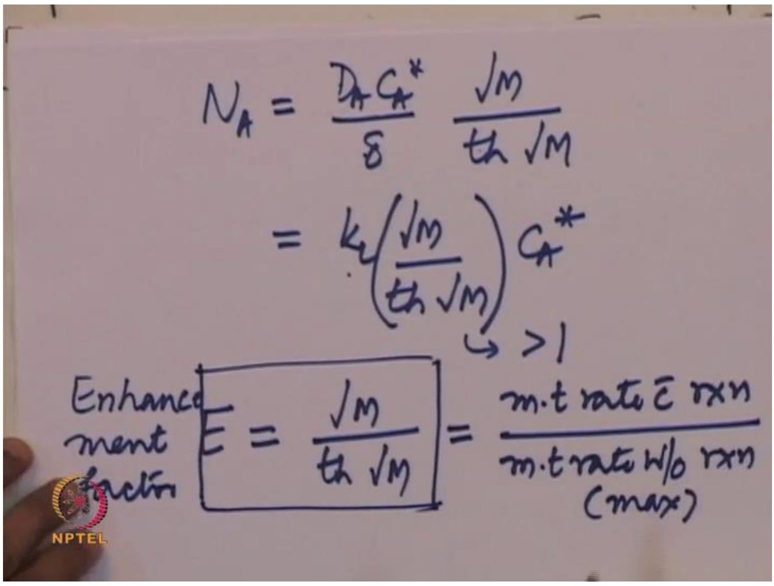

$$N_A = \frac{D_A C_A^*}{\delta} \frac{\sqrt{M}}{th\sqrt{M}}$$

$$= k_L \left(\frac{\sqrt{M}}{th\sqrt{M}}\right) C_A^*$$

$$\hookrightarrow > 1$$

Enhancement factor $\boxed{E = \frac{\sqrt{M}}{th\sqrt{M}}} = \frac{m.t\ rate\ \bar{c}\ rxn}{m.t\ rate\ w/o\ rxn\ (max)}$

.

Therefore, if ab is equal to 0 then we get NA as DA CA star divided by delta into root M divided by tanh root M. Recalling that DA divided by delta is nothing, but the mass transfer coefficient then we have we can write this expression in the following manner: which shows that the physical mass transfer rate which was kl time CA star is now modified by this factor root M by tanh root M. If you look at the values of tan h root M it turns out that tanh root M is usually less than root M.

Therefore, this factor has a magnitude more than 1 and tanh root M becomes 1 once root M exceeds values of 3 and so on. So, this is usually a factor that is more than 1. So, what we are saying is the absorption flux is more than the physical absorption flux by this factor and we call this factor as the enhancement factor. The definition and the expression for the enhancement factor is, this and this is the mass transfer rate with reaction divided by mass transfer rate without reaction.

So, here we consider the mass transfer rate without reaction under the maximum driving force which is CA star that is when the bulk concentration is 0. So, this is an important expression that is the take own expression from this part of the lecture. So, let us try to gain a bit more of physical understanding into what is going on by looking at how these profile look we have derived this expression for the concentration profile of a and. So, what is the nature of those profiles and what can we learn by understanding the nature so, these profiles.

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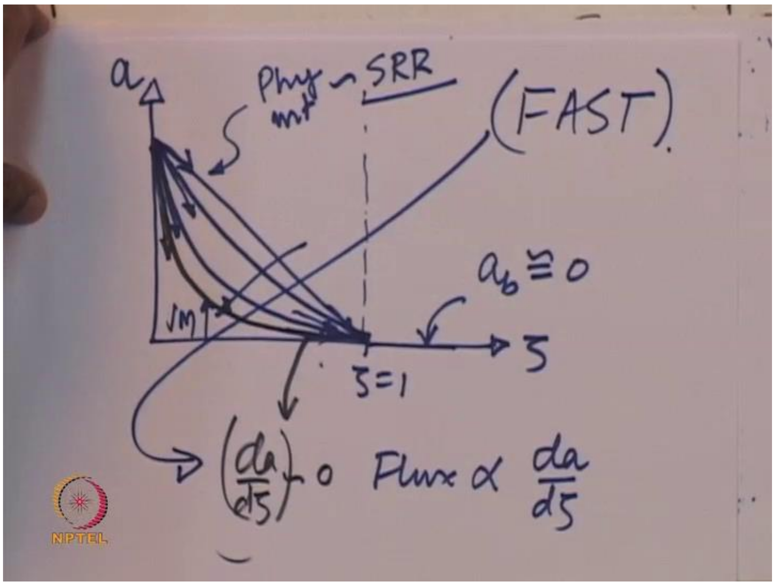

.

So, if you plot those profiles for different values of root M that is we are plotting the concentration of a as a function of zeta and this is zeta equal to 1 and that is the film region that we are talking about right. And let us, that is not worry too much about situations where ab is not equal to 0 that is assume that; ab is a approximately equal to 0. If it is not 0, if it its nearly equal to 0.

So, this is the physical mass transfer profile; linear profile and this is also true of slow reaction regime; when the values of root M were so small that we did not have to consider the rate expression at all in the diffusion equation. Now, the kind of expression that we have for the concentration profile that is this expression if you plotted this then it has a slight curvature here slight concavity. And the lager the value of root M the larger the value of this concavity so, this is root M increasing.

Now what does this mean? The flux at any point recall is proportional to the gradient right that is fix law. So, if the profile is linear what we are saying is the gradient at every point is the same therefore, the flux it this point is equal to the flux it this point. In other words, as much change of a is entering the gas liquid interface as is entering from the film into the bulk.

What happens to this in the bulk? It is reacted and all though as we have already said ab is nearly equal to 0.It is not exactly equal to 0 and because of the large volume of liquid that resides in the bulk even if the concentration of ab is very, very small it a counts for a significant amount of reaction which in fact, consumes all of this flux. So, that is a situation for slow reaction regime.

Now, under these circumstances what we are saying is that the flux here is proportional to that gradient, which is higher in absolute magnitude as compare to the flux at that point. So, the tangent at that point is steeper than the tangent at this point which means, more is entering at the gas liquid interface than is able to leave and this difference is being accounted for by the amount of that reacts within the film itself.

So, as root M increases this difference increases root m increases leading to more of a difference between the flux there and the flux here. So, more and more of the gas that is absorbed, but at the gas liquid interface is now by being consumed within the film itself. So, a logical end point to this sequence of profiles occurs when you come up with the profile that look something like this that is use the different color in order to illustrate this point.

So, ultimately you will come up with a situation where the concentration profile is such that this gradient da by d zeta is equal to 0. So, what is the implication of this? When root M is high enough for this to happen then, virtually all of the flux that is entering the gas liquid interface is being consumed within the film itself. Because, da by d zeta is 0 at the end of the film nothing is equal to going to the bulk.

So, the bulk liquid which is the recall that is about 1000 times in volume has compare to this is sitting they doing nothing. Because, no a is able to reach to the bulk at all; all the a that is absorbed is consumed within this. So, naturally this kind of a reaction qualifies to be called as a fast reaction. So, fast reaction is this situation here when the profile is so concave that it is gradient at the gas at the end of the film is equal to 0. The concentration profiles in fast reaction will therefore look something like this if you trace them for increasing values of root M.

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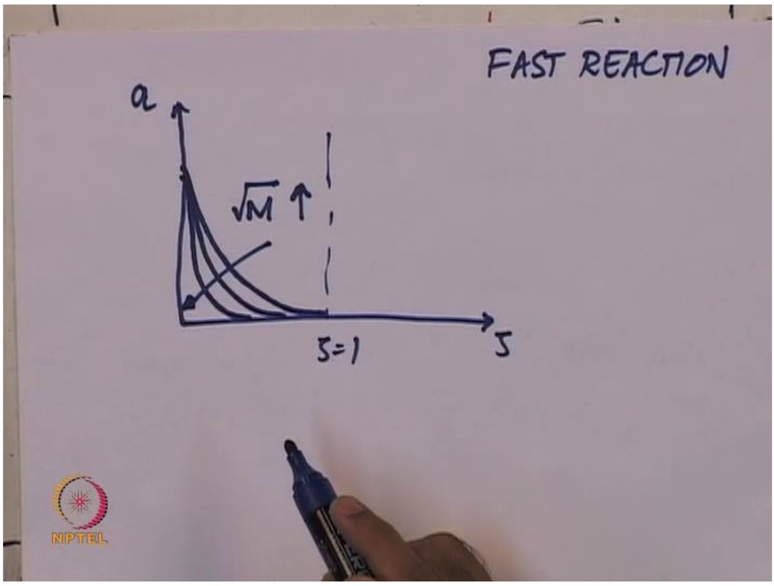

So, we are looking at fast reaction and this is the end of the film zeta equal to 1 and this zeta that is a. So, the in general the profile is going to 0 gradient somewhere within the film at just the start of the fast reaction regime. This happens at zeta equal to 1 for larger and larger values of the Hatta number we would expect the profiles to reside further and further into the film. So, this is the direction in which the Hatta number will increase.

So in other words, the entire flux of a that is entering into the liquid is being consumed more and more within the film as the value of the Hatta number increase. Now, clearly our formulation of the problem for the pseudo first order case which include at the first order reaction term on the right hand side. If you recall does not make any assumption about the concentration gradient being finished within the film or otherwise.

Therefore, this particular case to the fast reaction is embedded within the our formulation. So, our formulation must be able to predict this condition that we are discussing.

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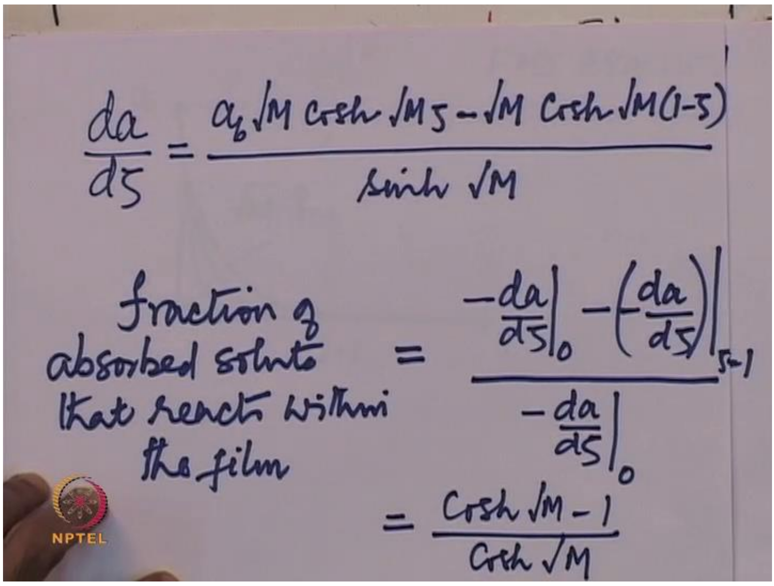

$$\frac{da}{d\zeta} = \frac{a_b\sqrt{M}\cosh\sqrt{M}\zeta - \sqrt{M}\cosh\sqrt{M}(1-\zeta)}{\sinh\sqrt{M}}$$

fraction of absorbed solute that reacts within the film

$$= \frac{-\left.\frac{da}{d\zeta}\right|_0 - \left.\left(-\frac{da}{d\zeta}\right)\right|_{\zeta=1}}{-\left.\frac{da}{d\zeta}\right|_0}$$

$$= \frac{\cosh\sqrt{M} - 1}{\cosh\sqrt{M}}$$

.

So, if you go back to the situation that we had considered earlier; this is the concentration gradient that we had defined earlier which is da by d zeta the non dimensional concentration gradient of a within the film be given by this kind of adsorption expression. Using this we can calculate the fraction of the solute that is being absorbed that actually reacts within the film in the following manner.

So, this is fraction of absorbed solute that reacts within the film is given by recalling that the flux is always proportional to the negative of the concentration gradient. We have minus da by d zeta evaluated at 0 this is the flux into the a film this what it is proportional to minus da upon d zeta evaluated at zeta equal to 1. This is the flux that is entering the bulk.

So, this difference is what is getting consumed within the film itself and that divided by the flux that is entering. So, this is clear the fraction of the absorb solute that reacts within the film. So, if you calculate these gradients from that expression over here and then, evaluate this expression it turns out to be cosh of root m minus 1 divided by cosh of root M.

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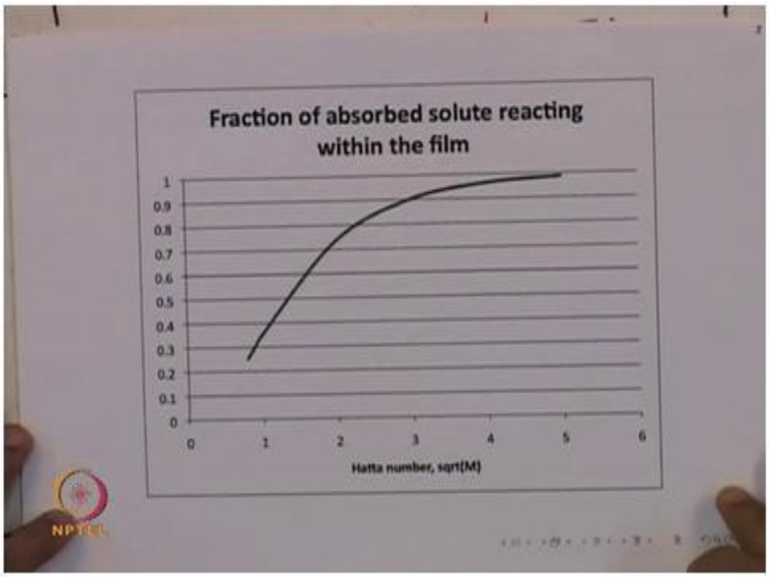

Now, this is this expression here this cosh of root M minus 1 divided by cosh of root M is plotted as a functions of the Hatta number in this figure here, where we see that as Hatta number varies from 1 onwards to higher and higher values the fraction increases continuously. And in particular if you look at the fraction that is absorbed for Hatta number values more than 3 that is root M more than 3 at root 3 at root M equal to 3 it is already something like 90 percent.

So, beyond that upwards of 90 percent of the reaction completely occurs within the film. So, this is a situation that we can call as fast reaction. So in other words, we identify the situation where virtually all the reaction that is 90 plus percent of the reaction is occurring within the a diffusion film is the situation of fast reaction.

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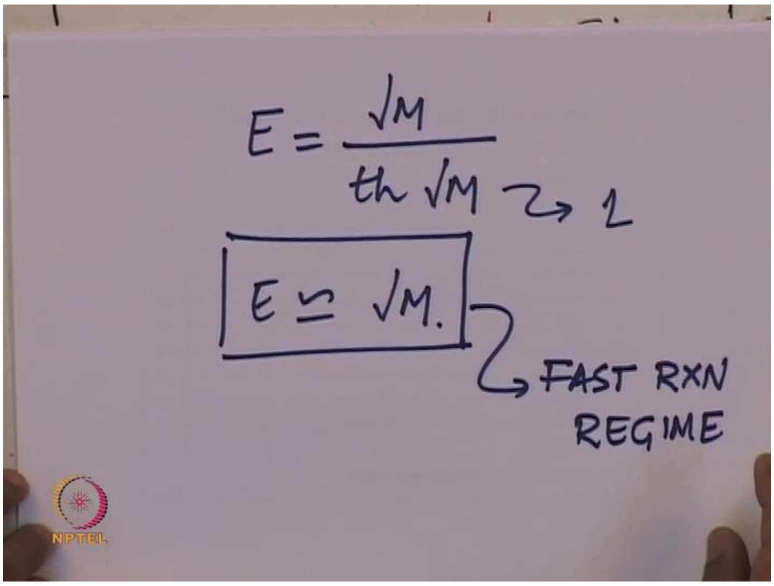

$$E = \frac{\sqrt{M}}{th\sqrt{M}} \rightarrow 1$$

$$\boxed{E \simeq \sqrt{M}.} \rightarrow \text{FAST RXN REGIME}$$

If you substitute at root M values of greater than 3 into this expression that we had the general expression that we had square root of M divided by tanh root M. Then, it turns out that the tanh of root M tends to 1 and therefore, e is approximately equal to root M. So, we can associate at this expression for the enhancement factor with the fast reaction regime.

Now, it is possible to approach the fast reaction regime from in other view point and that is by making use of the definition directly in the formulation of the problem. So, recall that we define the fast reaction regime as the situation and in which the reaction is complete within the film.

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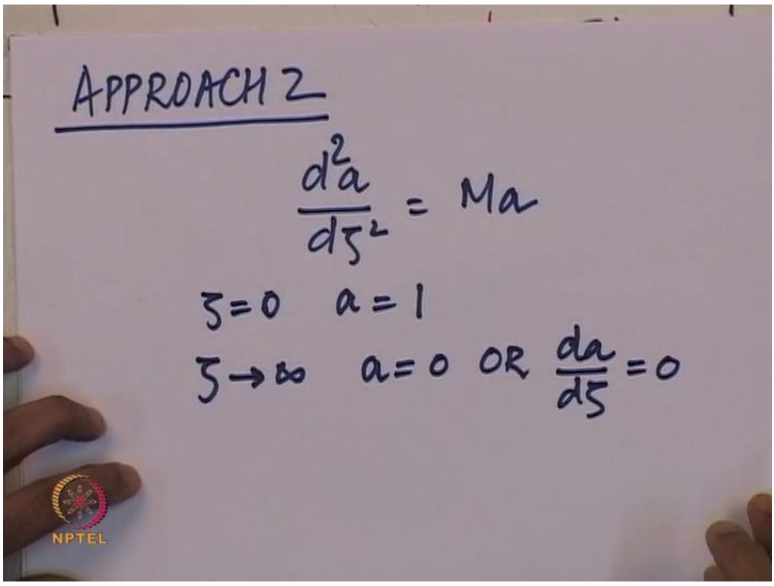

APPROACH 2

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

$\zeta = 0 \quad a = 1$

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

Therefore, we can write the governing equation so, this is what we may call as approach 2 to the case of fast reaction. So, from the definition we can write the following equation it is a same equation that is being solved, but it is now being solved in a situation where the first boundary condition is a same as before at zeta equal to 0, where a equal to 1. But the second boundary condition we can now replace, by the following condition we can say that zeta tends to infinity a equal to 0 or equivalently if it helps us we can use da by a zeta equal to 0.

So, what we are saying is that this is a situation in which because, the solute does not get to penetrate anywhere near the end of the film. The diffusing solute really does not nowhere the end of the film is it could as well be at infinity as for as the diffusing solute is concerned so much within the film the concentration as well as the flux go to 0 in this regime. So, if we solve this equation with the boundary conditions it is of course, the same equation that we are solving the same solution applies the exponential form the solution applies and so on.

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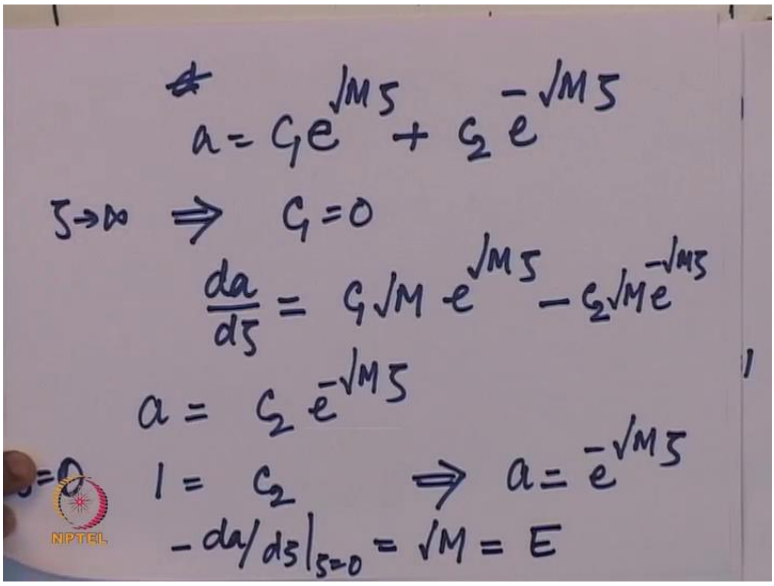

$$a = c_1 e^{\sqrt{M}\zeta} + c_2 e^{-\sqrt{M}\zeta}$$

$$\zeta \to \infty \Rightarrow c_1 = 0$$

$$\frac{da}{d\zeta} = c_1 \sqrt{M} e^{\sqrt{M}\zeta} - c_2 \sqrt{M} e^{-\sqrt{M}\zeta}$$

$$a = c_2 e^{-\sqrt{M}\zeta}$$

$$=0 \quad 1 = c_2 \Rightarrow a = e^{-\sqrt{M}\zeta}$$

$$-da/d\zeta\big|_{\zeta=0} = \sqrt{M} = E$$

.

And we have the solution being given by a equal to in terms of the 2 integration constants we have c1 e to the power root M zeta plus c2 e to the power minus root M zeta applying the zeta tending to infinity condition, we can say we come up with the value of the first integration constant that is c1 equal to 0. Because, what we are saying is that, zeta tends to infinity this term anyway goes to 0; when if this term is not to glow up then this constant has to be equal to 0.

And this conclusion can also be arrived at by saying that da by d zeta is 0 at zeta at zeta tends to infinity. Because, from the concentration profile differentiating this we have this equation for the concentration gradient; and the conclusion if you apply the condition that zeta tends to infinity da by d zeta goes to 0 would be no different from the case of saying that a goes to 0 under at the same point in the boundary in the a film.

So, either way we end of with this after applying this boundary condition and if we apply the further boundary condition at zeta equal to 0 which says, that a is equal to 1. Therefore, we come up with a equal to e to the power minus root M zeta as the solution to this equation with this pair of boundary conditions this time. So, with the this will give you that the negative of the gradient; which determines the flux is root M and if you substitute this in the expression for the enhancement factor this turns out to be exactly equal to the enhancement factor.

So, we arrived at the same conclusion 1 way or the other the first approach was to not make any assumption about the where the gradient of the a concentration profile is going to 0. Solve the equations in a general manner for the film theory and look at the limit, where the fraction of the solute that is actually being consumed within the film goes to nearly 1.

So, that situation leads to e equal to root M, we can alternatively formulate the problem itself in a manner that ensures this. That is we say that, the gradient well as the concentration of a go to 0 within the film and that also gives you the same result. So, the net result of this is that the formulation the problem now does not have a delta in it; that is the second approach that we took. The formulation the problem is completely independent of the film thickness and the film thickness is what comes from the film theory.

So, we suspect that the film theory kind of losses its significance of you know saying that we have a steady state process within operating within finite field 0 to delta. And the extent of this field that is magnitude of delta is determined by the hydro dynamic conditions in the bulk; in other words, the larger the intensity the smaller the delta and so on.

So, these things somewhat lose their significance because, if it is the value of delta that is being determined by the extent of turbulence or the hydro dynamic condition. And the value of delta is does not figure at all in the formulation of your problem we suspect that we get a situation here in which the absorption rate is independent of delta or equivalently the mass transfer coefficient.

So, this conclusion is rather far reaching it has some important conclusions which allow us to characterize the mass transfer contacting equipment in certain ways using the fast reaction regime. And this is not possible in other regimes have absorption and we will look at that in the next lecture.