

Chemical Reaction Engineering II
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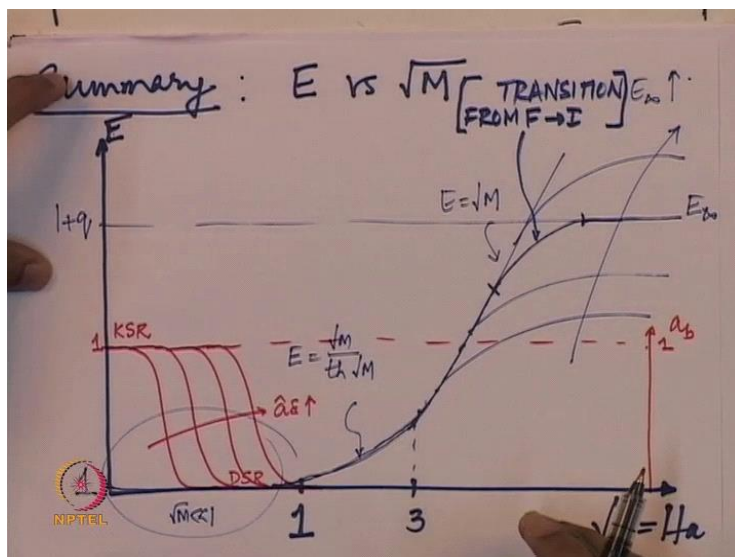
Lecture - 24

GLR-5: Transition to Instantaneous reaction; Reaction regimes in surface renewal Theories

In the last lecture, we continued our consideration of the effect of chemical reaction on mass transfer and completed a discussion of all the regimes. So, as the value of root m increases as we consider a reaction of increasing severity we first pass through the situation of slow reaction regime. In which the reaction is so slow that it is unable to influence the concentration gradients within the film. And then, we go to the fast reaction regime where quite in contrast to the slow reaction regime the reaction is virtually completed within the film itself.

Then the extreme case of reaction severity raises when the reaction is instantaneous in relation to mass transfer. In the sense that, it is a situation where a and b cannot co exist within the film. So, in that situation we saw that the reaction actually takes place at a single plane which is located somewhere within the film. And the location of the film itself is determined by the condition that the fluxes of a and b should match at the film with respect to the reaction stoichiometry.

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So, towards the end of the lecture yesterday we were considering the enhancement factor versus hatta number curve. And we saw that the curve generally has a shape of this kind when the value of the hatta number is very small we are in the slow reaction regime. The enhancement factor is equal to 1 that is to say that the mass transfer coefficient is equal to the physical mass transfer coefficient. And then as \sqrt{M} approaches a value of n the enhancement factor curve starts to level off. And when the enhancement factor when the value of the hatta number is more than 3 we enter into what we call as the fast reaction regime in which the bulk of the liquid is not carrying out any reaction at all.

So, the system proceeds along this asymptote where the enhancement factor is given by $E = \sqrt{M}$. And then depending on the value of q that is the relative abundant parameters that we have discussed earlier it settles down to 1 of these asymptotes as the value of the \sqrt{M} becomes much larger than q . So, this is the situation on this we can mark our regime this is the slow reaction regime this is transition from slow to fast reaction. In which the enhancement factor is given by that expression this is the fast reaction regime and depending on the value of q the system settles down in asymptotic enhancement factor equal to $E = \infty$.

So, that is the instantaneous reaction regime and this region here where the system has deviated from the fast reaction asymptote, but has not quite reach the instantaneous reaction asymptote. This we call as the region of regime of transition from fast to instantaneous reaction. So, this is a name that we can give to that regime. So, as you have seen we have got expressions for enhancement factor in all the regimes analytical expressions, within the framework of the film theory. So, here the enhancement factor is 1 here, it is given by that expression here; it is on this asymptote it is given by that expression.

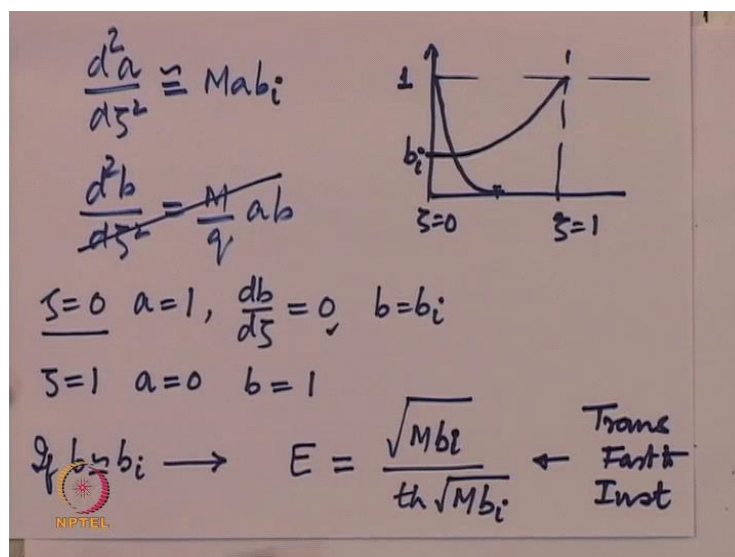
Here, it is equal to infinity this is the only regime the transition from fast instantaneous where we do not have an expression. But, knowing this asymptotes and that asymptotes we can do some kind of interpolation in order to track the codes of the enhancement factor. As \sqrt{M} increases in the transition regime we will in a moment derive an approximation solution to track that codes as well. But, for the moment all though we do not have a regress solution here it is possible to do an approximate interpolation between the fast reaction asymptote and the instantaneous

reaction asymptote. Just to complete the picture what we shall do is we shall edit an additional access here, which will track the concentration of the a in the bulk.

So, this of course, in the non dimensional terms this has a maximum value equal to 1 and the concentration of the a b is indeed equal to 1 in the kinetic sub regime or the slow reaction, as we have seen. So, its start there and it comes down and then attains value of 0 and then there after it remains 0. Now, at what value of root M does? The concentration decaying to 0 depends on another parameter, which we have called as the ratio of the film volume to the bulk volume. So, this is the direction in which this parameter $\hat{\delta}$ increases. So, depending on the value of a $\hat{\delta}$ you have a kinetic sub regime and you have a diffusional sub regime before the reaction starts influencing the proceedings within the film.

So, this kind of summarizes this plot now summarizes all we have discussed in the last we lectures in terms of the effect of chemical reaction on mass transfer, Now, before we leave this topic and go to see what the surface renewal theory is have to say about the reaction. Various reaction regimes are there any similarity what the film theory has to say and where are the differences and so on. We shall just address this transition regime where as we note it we do not have a regress analytical expression; because that regime involves the simultaneous solution of 2 ordinary differential equations which are coupled.

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So; obviously, you know that is not going to be an easy task and numerical solutions would be needed. But, a very clever analytical solution has been approximate analytical solution has been derived in the literature and because of the physical insides it gives into the transition regime we shall consider that briefly. So, we began our discussion by noting the that the equations that govern the transition regime are the second order differential equations; $D^2 a = M a b$ and $D^2 b = m / q a b$ with the boundary conditions $\zeta = 0, a = 1$ and $db/d\zeta = 0$.

Then $\zeta = 1, a = 0$ and $b = 1$. So, these are the boundary conditions that govern this; these equations and we also noted that in general the profile would look something like this. So, that is the film, this is your $\zeta = 1$ and $\zeta = 0$ the gas liquid interface and that is your concentration equal to 1 non dimensional concentration 1. And we noted that in general the profiles would look something like this the concentration profile of a goes to a 0 gradient, somewhere within the film. And then the concentration of b has starts with a 0 gradient at the interface and then it goes like that.

So, now what we note from this is that this the region where a and b are both present and much of the reaction takes place in the part of this region which is close to the interface. Because, that is is where the concentration of a is high. Now, we notice that because of this condition here the concentration profile of b is going to start with a 0 slope there, which means; for some small distance close to the gas liquid interface. The concentration of b is not very different from its interfacial value which we shall call as b_i . So, we are saying that $b = b_i$ at $\zeta = 0$ we of course, do not know the value of b_i .

But, if we knew the value of b_i a good approximation would be to consider the reaction to be fast order once again because the concentration of b is approximately equal to b_i . If you can make that approximation, then we do not have to solve this equation because after all what this equation gives is the variation of b with a distance. Which we now neglect and say that to a good approximation we can assume that in the regions where we are interested in tracking the concentration profiles b is substantially equal to b_i . So, if that is the case then of course, the equation becomes no different from the equation that we have already solved.

If b is considered approximately equal to b_i , then we have seen that we have already solved this first order equation. And that led to the situation that E is equal to root M divided by $\tan h$ root M . Except that, here instead of M we have M times b_i as the first order rate constant if like that multiplies the concentration a . So, this is an expression that we can use in the transition regime fast to instantaneous now that is all very fine except that, how do we know the value of b_i . And unless we knew the value of b_i we cannot of course, calculate the value of E .

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The image shows a whiteboard with the following handwritten equations:

$$\frac{d^2 a}{d\zeta^2} = q \frac{d^2 b}{d\zeta^2}$$

$$E = \frac{-D_A \left. \frac{dc_A}{dx} \right|_{x=0}}{+D_A \frac{c_A^*}{\delta}}$$

$$E = - \left. \frac{da}{d\zeta} \right|_{\zeta=0}$$

$$\zeta=0 \quad \left. \frac{da}{d\zeta} \right|_0 = -E; \quad b = b_i$$

So, in order to get the value of b_i we go back to our original equations here and note that in general whether we assume b as equal to b_i or not we can always write $d^2 a$ upon $d\zeta^2$ equals q times $d^2 b$ upon $d\zeta^2$. That is because if you look at these expressions the only difference between these 2 expressions is on the right hand side where on the in the side equation we are dividing by q . So, if we multiple by this equation by q the right hand become identical and we can then equate the left hand side. So, that is the equation that we have and we further note that the value of we know the gradient for b and we know the concentration for a .

So, what is the gradient for a . So, if we has that question then we see that $d a$ or let us consider the definition of the enhancement factor the enhancement factor is nothing but minus $d a$ $d c a$ upon $d x$ at x equal to 0 divided by minus $d a c a$ star or plus $d a c a$ star divided by delta which is

the physical mass transfer weight. So, the actually mass transfer weight in the present of chemical reaction as given by the solution of these equations divided by the physical mass transfer rate. So, that is the definition of e and.

So, canceling of $d a$ and making use of the use of the dimensionless numbers that we have dimensionless concentrations that we have defined earlier. We see that the concentration of gradient a in dimensionless terms at ζ equal to 0 is nothing but equal to the enhancement factor. So, we can use this and we shall of course, calculate denote the concentration of b at the interface as b_i . So, we can say we have additional conditions available now at ζ equal to 0. We can say that $d a$ upon $d \zeta$ at 0 is minus E that is this equation here and b equal to b_i of course, both of these are unknown at the stage.

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The image shows a whiteboard with the following handwritten equations and steps:

$$\frac{da}{d\zeta} = q \frac{db}{d\zeta} + D_1$$

At $\zeta=0$

$$-E = D_1$$

$-E = \frac{da}{d\zeta}; \quad \frac{db}{d\zeta} = 0$

$$\frac{da}{d\zeta} = q \frac{db}{d\zeta} - E$$

$$a = q b - E \zeta + D_2$$

$\zeta=0, a=0, b=1 \rightarrow 0 = q - E + D_2$
 $D_2 = E - q$

But, we shall see how we can relate these. So, starting with this equation and integrating it once we get $d a$ upon $d \zeta$ equal to $q d b$ upon $d \zeta$ plus a integration constant which we shall call as D_1 . Now, if we implement this boundary condition there then we know that at ζ equal to 0 we have $d a$ by $d \zeta$ is equal to minus E $d b$ by $d \zeta$ is 0. So, I am implementing the boundary condition at ζ equal to 0 and I am saying that at this point E is or minus E my concentration gradient of a and b is or rather the concentration gradient of b is 0.

So, this concentration becomes equal to d_1 and therefore, this equation becomes d_1 upon $d_2 \zeta$ equals $q d_2 b$ upon $d_2 \zeta$ minus E . So, now, we can integrate this once again and that gives us a equal to q times b minus E times ζ plus a . Second integration of constant which we shall call as d_2 . So, now, we apply the boundary condition that at ζ equal to 1 we have a as 0 and b is 1. So, this gives we put a equal to 0 and $q b$ is 1 minus e plus d_2 or d_2 is E minus q .

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$$a = qb - E\zeta + E - q$$

$$\zeta=0, b=b_i \text{ and } a=1$$

$$1 = qb_i + E - q$$

$$\text{or } b_i = \frac{1+q-E}{q}$$

$$E_\infty = 1+q \Rightarrow b_i = \frac{E_\infty - E}{E_\infty - 1}$$

So, substituting this back in the expression for a that is in this expression here we have a as $q b$ minus $E \zeta$ plus E minus q . So, this is the concentration profile of a in terms of the concentration profile of b . So, of course, in this equation we do not know the value of E . So, we bring in the additional condition that at ζ equal to 0 we have b equal to b_i and a equal to 1 all right. So, that is 1 equals $q b_i$ minus this terms goes plus e minus q or this is the equation that gives us the value of the concentration of b at the interface which is nothing but 1 plus q minus E divided by q .


So, we can write this in terms of since we are trying interpolate between the instantaneous reaction and the fast reaction regime. We can note that E infinity is 1 plus q which implies that b_i can be written as e infinity minus E divided by E infinity minus 1 .

(Refer Slide Time: 18:52)

TRANSITION FROM FAST \rightarrow INSTN.

$$E = \frac{\sqrt{M \frac{E_{\infty} - E}{E_{\infty} - 1}}}{\tanh \sqrt{M \frac{E_{\infty} - E}{E_{\infty} - 1}}}$$

— Implicit in E



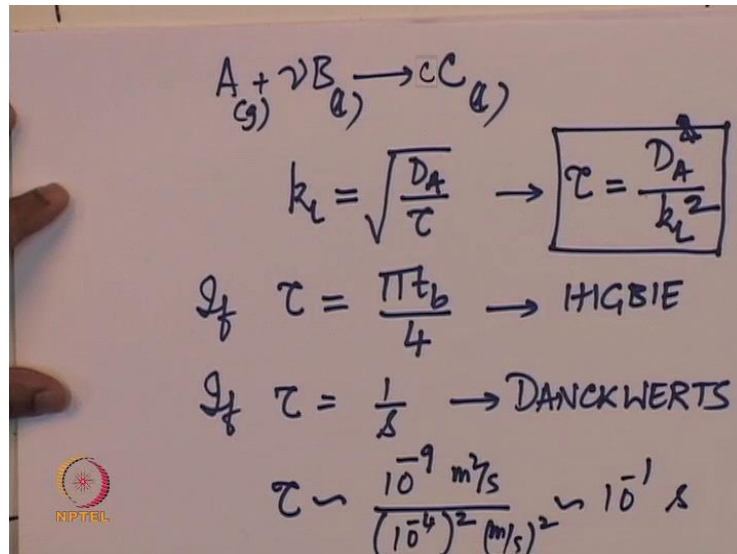
So, going to back to this expression now, for the enhancement factor E we can substitute the value of b_i and finally, conclude with this equation E. So, this is equation that governs the transition from fast to instantaneous. So, E is given by square root of $m b_i$ is $E_{\infty} - E$ divided by $E_{\infty} - 1$ divided by \tanh of same quantity $m b_i$ is $E_{\infty} - E$ divided by $E_{\infty} - 1$. So, this is an implicit equation that allows the calculation of E that is because E occurs in a transcendental form.

However, in most cases the \tanh term in the transition from fast to instantaneous the \tanh term goes to 1. And if that is the case you can take E equal to the nominator and square both sides end up in a quadratic which can be solved. So, if you are trying to solve this equation by try and error you can start with the solution. That obtains by assuming that the denominator is equal to 1 with that as the starting or the initial guess you can do newton raphs. And other methods of solving these kinds of equations you can implement 1 of those methods with the initial guess given by the equating nominator with E.

So, we now have an approximate way of calculating the enhancement factor in the transition regime as well as. So, no matter what our regime is we now have a way of calculating the absorption rate because once you know the enhancement factor you multiple the physical mass transfer rate with the enhancement factor. And you have the absorption rate for that regime. So,

that completes the discussion of the various reaction regime within the framework of the film theory.

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So, now, we address the question of whether you know we are just estimate at all in using the in the using the film theory. And that we do by considering the same regimes or considering the same situation of mass transfer occurring with a chemical reaction with a second order chemical reaction of the stoichiometry. A plus mu b going to c a is the in the gas phase b is in the liquid phase and let us assume that is in the liquid phase as well. The same reaction taking place in the in the liquid a is getting transported from the gas to the liquid, but now we assume that that transport is govern by a surface renewal type of mechanism.

So, in other words to recall the surface renewal mechanism there is a bulk that is in a state of churning in a state of agitation. And because of this agitation the surface element the elements of liquid from the bulk are thrown on the gas liquid interface; each element spends a certain length of time at the gas liquid interface. And during this time it is absorbing gas from the interface and while we did not consider the chemical reaction when we consider this picture in the context of physical mass transfer. Now, we shall consider chemical reaction in other words the surface element has going on within it a process of unsteady state mass transfer accompanied by a chemical reaction.

So, this process goes on and it leaves a certain concentration of a and concentration of product in the element by the time it leaves the gas liquid interface. And then these concentrations are even doubt as the surface element gets completely mixed within the bulk of the liquid. Now, we have seen that there are differences as to you know what is assumed for the distribution of residence time or distribution of surface ages. You know as given by the Higbie theory and as given by the Danckwerts surface renewal theory. But, in order to keep matters simple we shall take the attitude; we shall take the Stans that k_l is given by square root of d by some quantity with dimension of time which we should call as τ .

So, we note that, if τ is $\pi t b$ divided by 4 we have the Higbie postulate in which every element of liquid is spending exactly the length of time given by $t b$ at the interface or if τ is given by 1 over s . The surface renewal a surface renewal rate of surface renewal frequency then we have the Danckwerts picture. So, both of these theory can be combined in this manner into 1 expression which gives that τ is this is the incidentally. So, $d a$ squared divided by k_l so this $d a$ divided by k_l squared. So, this is the definition of the time that is time defined by this equation.

If you substitute the orders of magnitude for diffusivity which is of the order of 10 to the power minus 9 meters square per second usually and k_l is of the order of 10 to the power minus 4 squared. So, that is meter per second squared we note that this is of the order of 10 to the power minus 1 second. So, that is the order of magnitude of this characteristic time that we have defined by looking at the experimental mass transfer coefficient. So, that is 1 circumference we make use of the other 1 is that we have already made use of the expression for the Hatta numbers. In terms of the physical mass transfer coefficient rather than in terms of δ in terms of which we had 1st defined it.

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$$\sqrt{M} = \frac{1}{k_c} \sqrt{D_A k C_{Bb}}$$

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - k C_A C_B$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} - \nu k C_A C_B$$

$t=0$ all x , $C_A = C_{A0}$, $C_B = C_{B0}$ -
 $t > 0$ $x=0$, $C_A = C_A^*$, $\partial C_B / \partial x = 0$
 $x \rightarrow \infty$, $C_A = C_{A0}$, $C_B = C_{B0}$ -

So, if you look at this expression now there is nothing in it to suggest that the film theory postulate are in any way involved because of film theory construct, which is the film thickness has been eliminated in favor of mass transfer coefficient which is an experimental parameter. So, we will keep these 2 things in the background that is the definition of root M in terms of the mass transfer coefficient. And a characteristic time, that is calculated by reference to the experimental mass transfer coefficient which is of the order of 10 to the power minus 1 second.

So, the governing differential equations for the case of you know a second order reaction accompanying mass transfer would be can be written down in that manner $D_A \frac{\partial C_A}{\partial t}$ equals $D_A \frac{\partial^2 C_A}{\partial x^2}$ minus $K C_A C_B$. So, what is this is saying is that accumulation within a differential element within located within the surface element is equal to the input minus output minus consumption by chemical reaction. So, when we last considered the surface renewal theory in the context of physical mass transfer this reaction term was not there. It now makes it appearance because we are now considering the effect of chemical reaction on mass transfer.

Similarly, for b we have this equation $D_B \frac{\partial C_B}{\partial t}$ equals $D_B \frac{\partial^2 C_B}{\partial x^2}$ minus $\nu K C_A C_B$ which is the rate of consumption of b within the surface element. The initial and boundary conditions that are applicable are at t equal to 0 that is initial condition for all values of x .

Everywhere within the surface element we have the concentration of A as equal to the concentration of bulk, where the element is coming from and the concentration of b is equal to the concentration of b in the bulk. In other words the surface element is taken out of the bulk liquid.

Therefore, when it just comes to the interface nothing has changed within the surface of the element at t greater than 0 we have 2 conditions at x equal to 0. We have C_A equals C_A^* in equilibrium with the prevailing partial pressure on the gas side and we have dC_B upon dx equal to 0. And at large distances from the interface which we call as extending to infinity because the element is pending fraction of a second at the interface. There is not enough opportunity for the gas to diffuse very much deep into the surface element. Therefore, we can regard the surface element as infinitely deep from the point of view of the diffusing salute.

So, we have C_A bulk and C_B bulk in other words the conditions at x tending to infinity for large times for times larger than 0 are identical to the conditions at all x at t equal to 0. So, this as we have noted earlier suggest a combination of variables which we will come to in a in a minute. But, before we do that as usual we want to minimize our work of having to solve these complicated partial differential equations where which are which are coupled. Therefore, rather than go to the computer and starts solving these by methods of brute force we shall do dome analysis by 1st non dimensionalizing these equations.

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Non-dimensionalization

$$a = C_A / C_A^*, \quad b = C_B / C_{Bb} \quad \text{Chc. dist}$$
$$\xi = x / \sqrt{Dt}$$
$$\tau \rightarrow \theta = t / \tau$$
$$\downarrow$$
$$= \frac{D_A}{k^2}$$
$$\text{Ch. } \xi = \sqrt{Dt}$$
$$\text{Ch. } \xi = \sqrt{D\tau}$$

So, in non dimensionalization we have no difficulty in defining a non dimensionalization concentration A because we have already done that in the context of film theory. And we similarly can find defined a non dimension concentration b again in identical terms to what we did in the context of film theory. But, when it comes to a non dimensional distance we note that there is a bit of problem because the field of diffusion is semi infinite. In this case it is bounded on 1 side by the gas liquid interface, but on the other side it goes to infinity.

So, this problem as no characteristic length so; however, we note that there is a characteristic time for the process that is tau, which we have defined by looking at the physical mass transfer coefficient. And in terms of tau a dimensionless time can always be defined and that is t divided by tau where tau we have seen is D_A divided by k^2 . And we note that a characteristic distances can be calculated from this characteristic time by reference to the equations of physical mass transfer.

You recall the error function solution we derived for the concentration profile as a function of distance and time in the physical mass transfer case. And if you plug in the you know x is equal to square root of dt, in that equation. Then it shows that this is the depth to which approximately the salute will penetrate in a time t that is, because if you plug this condition into the error

function complement solution. It shows that, the significant part of the concentration profile lies within this distance.

So, this can be made use of as a characteristic distance that is the characteristic depth of penetration by substituting the characteristic time in this expression. So, x equal to square root of d tau will be our characteristic x with that we can define a dimensionless a distance as x divided by square root of d tau. So, we have now ready to go through with the non dimensionalization of our equations and if we do that for A we have the flowing equation. We have this equation for A and this is the 1 that i am considering right now.

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$$\frac{C_A^*}{l} \frac{\partial a}{\partial \theta} = D_A \frac{C_A^*}{l^2} \frac{\partial^2 a}{\partial z^2} - k C_A^* C_B^* a b$$

$$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial z^2} - (k C_B^* l) a b$$

$$M = \frac{1}{k l^2} D_A k C_B^* l$$

$$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial z^2} - M a b$$

So, we have CA star da divided by d theta divided by tau here and DA CA star divided by the characteristic distance comes out here raised to the second power, because we have a second derive here. And therefore, that is d a tau minus k times CA star CB bulk ab all right. So, getting rid of all the variables from the left hand side we have da upon d theta d a will cancel here and CA star upon tau will cancels there. So, we have d square A upon d zeta square minus k CB b tau multiplied by ab. Now, recalling that tau is nothing but d a divided by kl squared. So, this term is 1 upon kl squared da k CB b. So, this shows that this is nothing but square of the Hatta number itself written in terms of the mass transfer coefficient.

So, our equation now becomes $\frac{D_A}{D_B} \frac{\partial b}{\partial \theta} = \frac{\partial^2 b}{\partial \zeta^2} - \frac{M}{q} a b$ which shows that the effect of any effect of that the chemical reaction has on the concentration profiles. So, these terms would be absent and in physical mass transfer. So, any effect that the chemical reaction has on the concentration profile has to be understood in terms of the magnitude of the dimensionless parameter M . So, what is this M , M is of course a same quantity that we have visited earlier, but if we want we can interpret m in terms of the postulates of the surface renewal theories. So, M nothing but $k C_B \tau$.

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$$M = k C_B \tau$$

$$\frac{D_A}{D_B} \frac{\partial b}{\partial \theta} = \frac{\partial^2 b}{\partial \zeta^2} - \frac{M}{q} a b$$

$$\theta = 0 \quad \text{all } \zeta \quad a = a_b, \quad b = 1$$

$$\theta > 0 \quad \zeta = 0 \quad a = 1 \quad \frac{\partial b}{\partial \zeta} = 0$$

$$\zeta \rightarrow \infty \quad a = a_b \quad b = 1$$

So, it is some kind of Damkohler number in that sense because $k C_B \tau$ is the first order rate constant and that is the time required for the reaction to proceed to a significant extent. And τ is the time that is available for reaction to occur because after time τ typically characteristically the surface element sees us to be at the surface. So, naturally if large values of m corresponding to significant amounts of reaction taking place within the life of the surface element. And small values of M corresponds to a negligible amount of reaction taking place within the a life of the surface element.

So, that is as for as m is concern. So, we can do a similar non dimensionalization as we did for the case of a for the case of b_i shall leave the details to you. But, basically the equation that results is something like this M up on $q a b$. So, just as in the case of film theory you note that m

upon q is making an appearance in the reaction term here where as M appeared in the equation for a the other difference. That we note from the case of film theory is that the ratio of diffusivities a to b is appearing in this equation. Whereas, that was not a parameter a that appeared anywhere in the in our considerations in the film theory.

So, that will have some consequences as we go along, but for the moment we shall continue with this and write down the initial and boundary conditions in terms of the non dimensional parameters. The initial condition is at θ equal to 0 for all values of ζ you have a is ab which is the ratio of the concentration of a in the bulk to CA^* and b is 1. Because, the element is coming from the bulk and for values of time greater than 0, that is once the element has landed at the interface at ζ equal to 0. Then you are a is 1 and db upon $d\zeta$ is 0 and as ζ tends to infinity we have a going to a/b and b going to 1 and these 2 conditions are similar.

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Case 1: $M \ll q$

Eq (b) $\frac{D_A}{D_B} \frac{\partial b}{\partial \theta} = \frac{\partial^2 b}{\partial \zeta^2} - (\text{in } 0)$

$\eta = \frac{S}{2 \sqrt{\theta D_B / D_A}}$

$\frac{\partial b}{\partial \theta} = \frac{db}{d\eta} \frac{\partial \eta}{\partial \theta}$ and so on

Now, so we have these equations we have the equation for we have equation for a and the equation for b with the applicable initial and boundary conditions and let us consider these equations in terms of increasing severity of m . So, the q parameter that appear is the relative abundance parameter that we have already seen in the in our consideration of film theory. And we have noted that q is usually a number that is much larger than 1. So, that continues to be case

here. So, we shall first consider the case where for value of m is much larger small than q . So, we are considering very slow reactions for which the value of M is small any way.

Then considering that q is usually large number we are approaching the matter of the effect of chemical reaction on mass transfer from a point of view a from the point where the reaction is very slow. Now, if that is the case then the equation for b becomes D upon DB db upon d theta equals d squared b upon d zeta squared, because the other term is close to 0; the term that contains the ratio of M to q . Now, in the case of film theory the moment this assumption was made it fell out that b is equal to 1 everywhere within the film. We did not have to do much work we should persist with the equations of surface renewal theory for a bit.

If only to demonstrate that there is a lot more work involved in arriving at similar conclusions as we arrived at in the case of film theory. But, within the framework of surface renewal theory surface renewal theory is a transient theory the equations are partial differential equations the film theory is a steady state theory the equations are ordinary differential equations. So, we shall see how things were come. So, a conclusion that was self evident in the case of film theory will be made with considerable effort in this case.

So, we need to it is not clear from this although in an intuitive sense since we are saying that the reaction is slow and the relative supply of b relative to the h rate at which it is required by stoichiometry is much larger than 1. So, a combination of these 2 circumstances should mean that the concentration of b is uniform right up to the interface at all times in the case of the surface element. But while that is intuitively obvious the mathematic should also its says the same thing and it is not obvious whether this equation is saying the same thing. So, we shall solve this equation once again by combining the variables manner in which we did it for the case of physical mass transfer.

We can define a a combination variable η and I shall directly write the equation for η . So, if you make this substitution here calculate these derivatives in terms of η for example, you can say that d upon d theta is d a upon d eta and d eta partial d eta upon d theta so on. So, we can work out all these sorry this is i should have b there. So, we can work out all these derivatives on both sides by these kind of application of chain rule of differentiation. And if we did that and

wrote down the final equation we see that theta and eta theta and zeta disappear from the equations leaving behind only eta.

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$$\frac{d^2b}{d\eta^2} + 2\eta \frac{db}{d\eta} = 0$$

$$\eta = 0 \quad \frac{db}{d\eta} = 0 = u \text{ (non volatility)}$$

$$\eta \rightarrow \infty \quad b = 1$$

$$u = \frac{db}{d\eta} \quad \frac{du}{d\eta} = -2\eta u$$

$$u = C e^{-\eta^2} \rightarrow C = 0$$

$$u = 0$$

So, this is the equation that results and the corresponding 2 boundary conditions for this ordinary 3 differential equation. Now, is eta equal to 0 is d b upon d eta equal to 0 this is this comes from non volatility of of b and as eta tends to infinity b equal to 1 this is the 2 conditions 1 for t equal to 0. And the other for extending to infinity, which can be combined because; under both of these conditions the concentrations are identical. So, we can integrate this in a straightforward because if we let u stands for db upon d eta the first derivative then this equation is du upon d eta equals minus 2 eta u which has a straightforward integral Ce to the power minus eta squared.

Then if we apply this boundary condition and noting that this is u at eta equal to 0 this term is 1 and we are saying u equal to 0. So, this application of the boundary condition this 1 shows that C equal to 0 which means u is 0. And if u is 0 db upon d eta is 0 and; that means, that b is a constant for all eta. And since b is equal to 1 at 1 value of eta that we know that we have this condition. So, this leads us to b equal to 1. So, we have to do ... So, much work to realize that the concentration of b is uniform throughout.

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$$\frac{db}{d\eta} = 0 \rightarrow b = \text{const for all } \eta$$
$$\underline{b = 1}$$
$$\underline{\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial \zeta^2} - Ma} \rightarrow \text{PSEUDO FIRST ORDER CASE}$$

So, once we when once we realize that we can now rewrite the equation for a as d upon d theta equals d square a upon d zeta square minus $M a$ because b is equal to 1. And this therefore, now becomes the pseudo first order case because the order with respect to b is degenerate. And therefore, we have this equation here once again within the pseudo first order case, we will first consider where we are considering case 1 which is pseudo first order regime or pseudo first order case.

(Refer Slide Time: 46:34)

Case 1 A) $M \ll 1$

$$\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial \zeta^2} \rightarrow \text{PHY M.T.}$$

MT Coeff = Phy MT Coeff

→ identical concl. to the Case of F.T.

We shall now consider under case 1 a, which is m being for less than 1 it is not only for less than 1 q it is additionally for less than 1. So, in this case we have d_a upon d theta is equal to d square a upon d zeta squared there is no appearance of the chemical reaction term anywhere in the works. And we have the equation and initial and boundary conditions which are identical to the case of physical mass transfer. So, in another words what we are saying is that the reaction is sufficiently slow in this case, that from the point of view of the surface element. Which is spending time at the gas liquid interface; the reaction is enabled to make any dent in the concentration profiles.

And therefore, the concentration profiles will work out to be exactly the same as in the case of physical mass transfer which means we have the error function complements solution applying and we arrive at the instantaneous flux which we average with respect to the weighted with respect to the surface age distribution and so on. So, everything works out in an identical manner to the case of physical mass transfer, so the mass transfer rate or mass transfer coefficient is not influenced by chemical reaction. This is equal to case of physical mass transfer coefficient.

So, this conclusion is identical to identical conclusion to the case of film theory all right. So, now, we has the question then what is the role of chemical reaction here and we come up with the answer that in order look for the effect of chemical reaction. Now, we have to look at what is happening in the bulk because that is where the reaction is actually occurring. So, we make a bulk balance and again we have to anticipating that the volume of the liquid in the surface elements is going to be much smaller than the volume of element volume of liquid in the bulk. We can write the bulk balance in a manner that is identical to the case of what we did when we were discussing film theory.

(Refer Slide Time: 49:09)

$$V_L k_L \hat{a} (C_A^* - C_{Ab}) = V_L k_{Cb} C_{Bb}$$

$$a_b = \frac{1}{1 + P}$$

$$P = \frac{k_{Cb} C_{Bb}}{k_L \hat{a}} = \frac{M}{\hat{a} \sqrt{D_A \tau}}$$

Vol of liq within the penetr depth
Total Vol of liq $\sim O(10^{-3})$

So, this is the rate of mass transfer per unit liquid volume multiply that by the liquid volume and that is the we should have had the volume here. But, we are using the liquid volume here. So, this is equal to v_L into k into C_{Ab} times C_{Bb} . So, this is the same equation has we did earlier and therefore, this will of course, lead to this equation that the bulk concentration of a is equal to 1 plus p where p is $k C_{Bb}$ divided by k_L . We had shown this as equal to m divided by $a \Delta$ here in the case of film theory and in this case it turns out.

If you do the manipulations that it is it is this quantity where the quantity within the in the denominator is nothing but the volume of liquid within the penetration depth penetration depth divided by total volume of liquid. Since this is the same equation that same expression that we are dealing with this. You can plug in the actual numbers τ is equal to minus 10 to the minus 1 d is 10 to the power minus 9 so and so forth. And this turns out to be of the order of 10 to the power minus 3 all right.

So, all this to just say that in the event of m being much less than 1 there is virtually no difference between what the film theory has to say and what the surface renewal theories have to say. So, this you know which variant of the surface renewal theory you are considering does not really matter because the mechanism of mass transfer itself is such that the reaction does not have any influence. And therefore, whatever remarks we made for the surface the Higbie version

of the surface renewal theory versus the Danckwerts version of the surface renewal theory in the case of physical mass transfer. Those remarks apply identically, in this case when we come to the considering the effect of mechanically reactions it centers on the value of this parameter p .

Then the value of parameter p can be either much greater than 1 or much less than 1 both of these conditions are possible. Because, the volume of the liquid that is contained within the surface element within the penetration depth is much smaller than the total volume liquid, there is in the tank. And with that understanding both p much greater than 1 and p much less than 1 or possible, so in 1 event we have the kinetic sub regime in the other event we have the diffusional sub regime.

So, up to the end of the slow reaction regime we are solving i mean our solution of the surface renewal theory equations; gives us nothing different from whatever we have concluded from our consideration of film theory. So, what happens for faster reactions is something we will take up in the next lecture.