Chemical Reactions Engineering II
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Lecture - 6
GLR-7: Surface renewal theories: Instantaneous reaction and Summing up

Welcome back. We have been considering the effect of chemical reaction on the mass transfer rate, within the frame work of the surface renewal theories.

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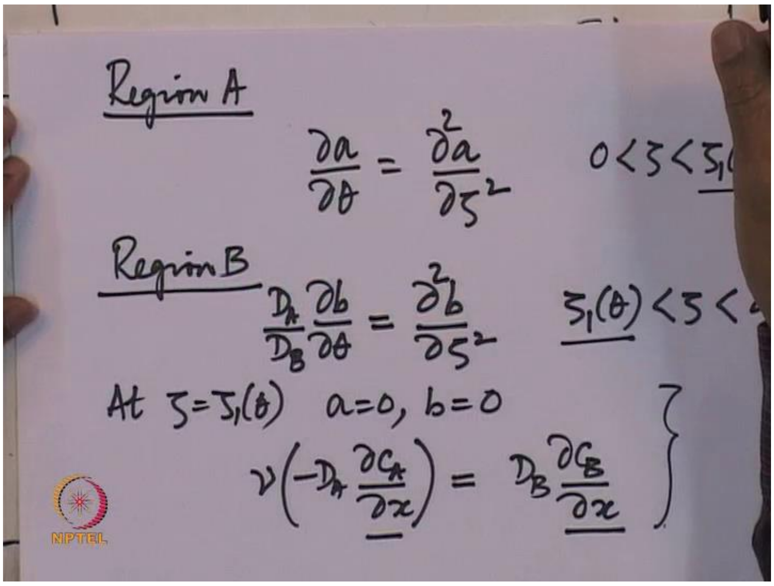

Region A

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

Region B

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

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

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

And in the last lecture, we set up the equations in the frame work of these theories that describe the instantaneous reaction regime. So, you recall that, these were the equations. So, the instantaneous reaction regime is 1 and which A diffuses from the interface and B diffuses from the bulk. And they meet and consume each other at reaction plane, which is locate at somewhere within the surface element.

So, these reactions plane itself, starts at the gas liquid interface. At the instant, the liquid element arrives at the gas liquid interface. And as the element ages at the interface, as it spends more and more time at the interface; the reaction plane progressively moves inward into the liquid element. So, this becomes a moving boundary problem. And if you look at the equations that set up, so there is a region between 0 and zeta 1 of theta, where zeta 1 is location in non dimensional terms of the reaction plane.

So, the region between 0 and the reaction plane; the interface and the reaction plane, is occupied by A. And since there is no B, there cannot be a reaction there. So, it is a case of pure diffusion. The region between the reaction plane and the rest of the element is occupied by B and once again, since there is no A there they cannot be reaction and this is the equation that governs the pure diffusion of B in that region. At the reaction plane itself, because the reaction is assumed to be instantaneous, the concentration of A and B both go to 0. And the rate of supply of B from the in the negative x direction if you like, is in psychometric requirement as compare to the rate of supply of A in the positive x direction. So, that is why there is a sign difference here.

So, now, this is the formulation of the problem. And in order to solve this, we require a little more information. And that is, because this is a moving boundary problem, we need to track the boundary movement. Now this can be done in various ways. And bird Stewart lightfoot in there, in the 1st edition of their book: Transport Phenomena, suggest a very elegant to way of doing this. And we will simply state that before proceeding further.

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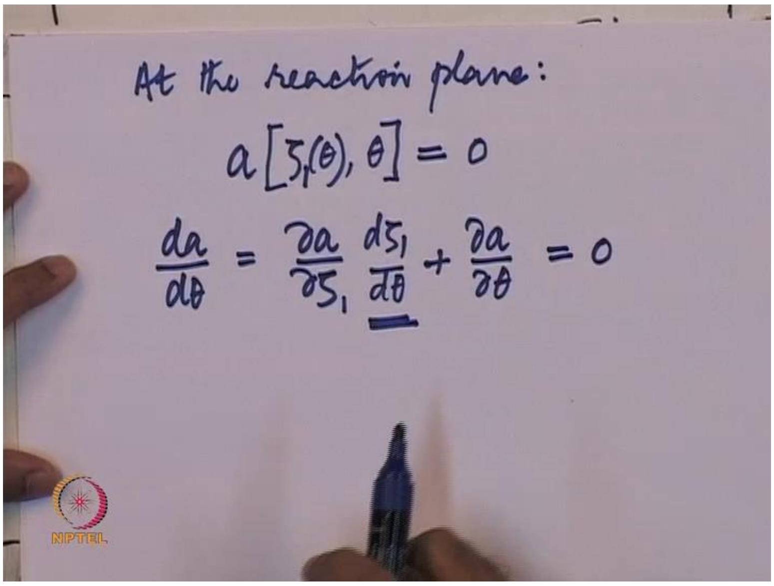

At the reaction plane:

$$a[\zeta_1(\theta),\theta] = 0$$

$$\frac{da}{d\theta} = \frac{\partial a}{\partial \zeta_1}\underline{\frac{d\zeta_1}{d\theta}} + \frac{\partial a}{\partial \theta} = 0$$

So, this approach, consist in recognizing that, at the reaction plane, the following identity holds. We have the concentration of a, which is a function of zeta and theta. And since you are considering the reaction pane, it is zeta 1 which is itself of function of theta is identically equal to 0. So, a at the reaction plane is a function of the single variable theta and that is a constant value and it is 0.

So, if it differentiate this we get, d a by d theta equals partial d a by d zeta 1 d zeta 1 upon d theta plus partial d a by d theta and this is equal to 0. And this gives you the equation for the boundary movement which is d zeta 1 by d theta. So, this can be rearranged to get the rate at which zeta 1 moves with theta and that equation can be used along with the previous 3 shown equations, in order to arrive at a solution, to these equations.

So, that solution is analytically possible. And it is the details of the solution are available in the books that I mentioned in the previous lecture; the book by Danckwerts, that is, Gas Liquid Reactions and the book on Transport Phenomena by bird Stewart and lightfoot. We will not go into the details of the solution except, to mention that the solutions looking at the nature of the equations; the solutions can be expected to be of the error function type.

So, we formulate the error function solutions, in terms of the variable x divided by or zeta divided by 2 root theta in non dimensional terms. And the constants are evaluated using the conditions that I have laid out earlier. So, now, it turns out when we solve these equations that, the rate of the instantaneous rate of absorption or the instantaneous flux, which is given by a negative of the diffusivity multiplied by the concentration gradient at the interface. So, this flux has the same kind of dependence on time, as the flux in the case of physical mass transfer.

In other words, if you look at the absorption rate, at every point during the life of the surface element, the absorption flux is greater than the physical absorption flux by a constant factor. Since this factor which enhances the instantaneous mass transfer rate is the constant, ultimately when you average these instantaneous rates, waited with the I of dt function; whether you assume the Higbie function or the danckwerts function for I of t dt that is the plug flow or the mix flow assumption at the interface. It does not really matter, as per as the effect of reaction on the mass transfer rate is concerned. Or in other words, in so far as the calculation of enhancement factor is concerned.

So, if you can define an instantaneous enhancement factor, which is the rate by which is the factor by which the instantaneous flux is higher than the physical mass transfer flux at every time during the life of the surface element, this instantaneous enhancement factor is independent of time. And therefore, the average enhancement factor over the entire life for the element, whether you average the enhancement factors using the Higbie function or the Danckwerts function, it gives you the same result. So, that result is what I will give you next.

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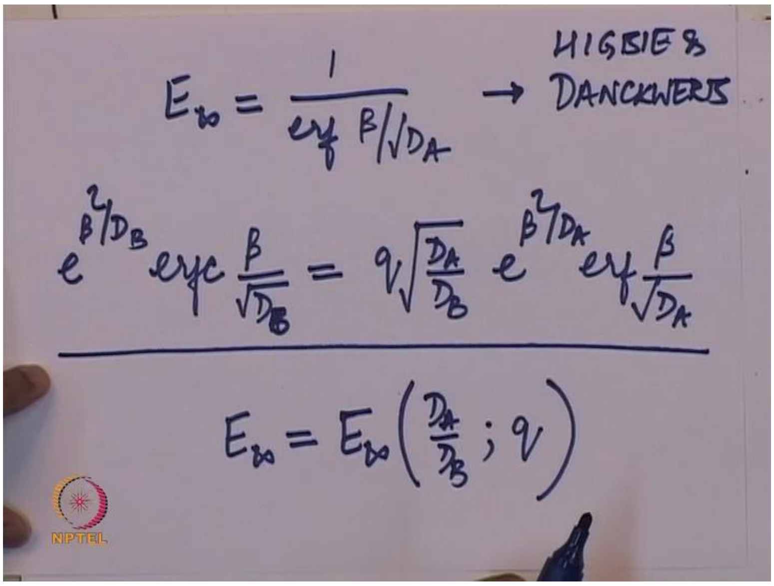

$$E_\infty = \frac{1}{\mathrm{erf}\,\beta/\sqrt{D_A}} \rightarrow \text{HIGBIE \& DANCKWERTS}$$

$$e^{\beta^2/D_B}\,\mathrm{erfc}\,\frac{\beta}{\sqrt{D_B}} = q\sqrt{\frac{D_A}{D_B}}\,e^{\beta^2/D_A}\,\mathrm{erf}\,\frac{\beta}{\sqrt{D_A}}$$

$$E_\infty = E_\infty\left(\frac{D_A}{D_B}; q\right)$$

So, that is given by an expression of this kind; error function of beta divided by square root of D A, where this function beta where this parameter beta comes from the transcendental function, exponential of beta squared divided by D B error function compliment beta divided by square root of D A equals D B rather q square root of D A upon D B e to the power beta squared by D A error function of beta divided by square root of D A. So, this is the equation that is implicit in beta, which has to be solved by a process of trial and error knowing the other quantities like q and D A and D B. And once you get beta, you substitute this in the enhancement factor expression. And this is the same expressions in both the surface renewal theories that we have considered; that is Higbie and Danckwerts.

So, the message that you have try to convey here is that, within the frame work of these theories is the surface renewal theories E infinity turns out to be or the maximum enhancement factor available to a system, turns out to be function of D A by D B and the parameter q. Recall that it was a function only of q in the film theory. And here it, there is additional parameter which is a ratio of diffusivities.

We have set that often this ratio is not very far from unity. The rate of I mean the diffusivity of A ratio with respect to the diffusivity of B is a number something like 1 in many cases. And in that in those situations, the E infinity becomes a function of q alone in the ambit of surface renewal theories, as it does in the case of the film theory. Moreover, there is also while these expressions look very different from the expression that, we obtained for the film theory. It turns out that, if the value of the enhancement factor is large, then there is a very simple approximation that obtains to this complicated expression here.

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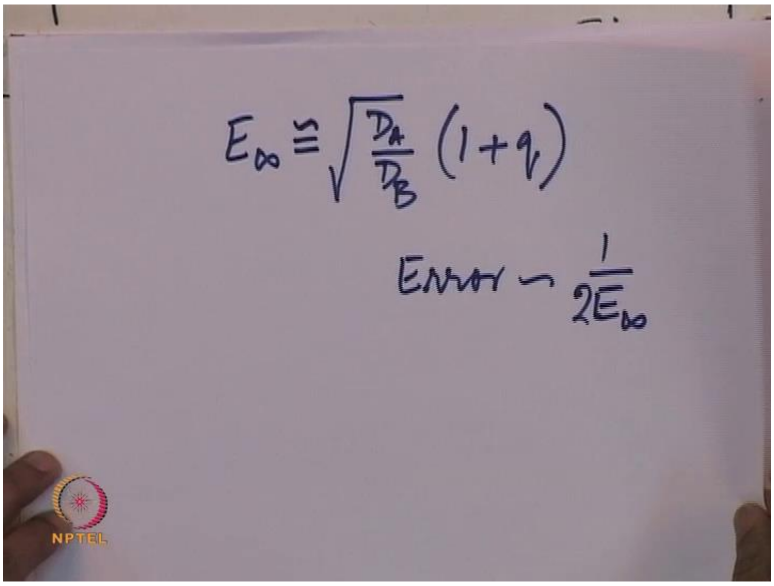

$$E_\infty \cong \sqrt{\frac{D_A}{D_B}}(1+q)$$

$$\text{Error} \sim \frac{1}{2E_\infty}$$

And that is E infinity equals square root of D A upon D B multiplied by 1 plus q. And if you recall, that without this diffusivity function, what remains; was the enhancement factor predicted in the instantaneous reaction regime by the film theory. So, the factor that distinguishes the surface renewal theory expression from the film theory expression is, just this factor square root of the diffusivity ratio. Now this is as I said it is an approximation. And the error that you make in a calculating enhancement factor by this expression; is of the order of 1 over to E infinity.

So, the larger the value of the enhancement factor is, in the other words larger the value of q is, the smaller the error that you make in using this expression. So, now we are in a we have gone through the entire gamest of regimes, in the surface renewal theory framework.

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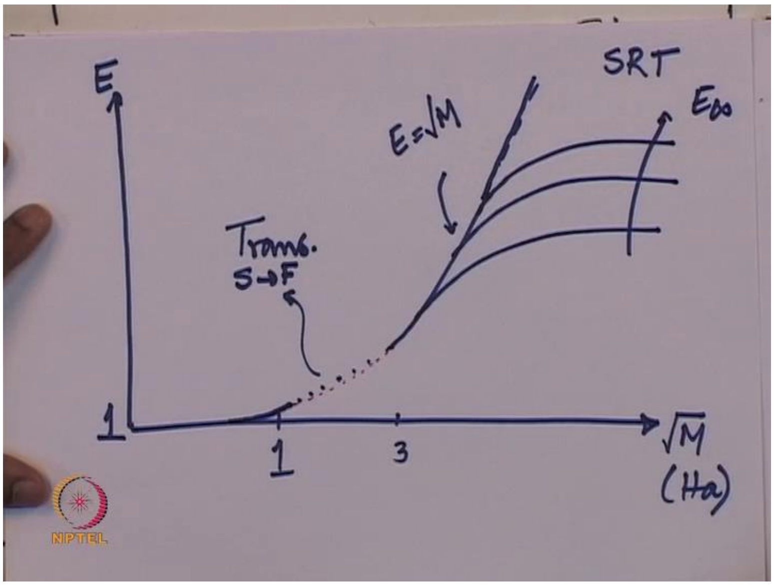

And we are now, in a position to put the entire story down, in terms of a plot of enhancement factor versus square root of M or also called as Hatta number. So, we have Hatta number of 1 somewhere there. Let us say Hatta number of 3 somewhere here. And so the enhancement factor remains 1. So, this is the story according to surface renewal theories.

So, this is the slow reaction regime, where we said that there is absolutely no difference between the surface renewal theories and the film theory. And about 1, the enhancement factors start to lift off to the ground. So, this is 1 and we have region here, which I will show by dotted lines, which is the transition slow to fast, where there is bit of difference between the film theory and the surface renewal theory.

So, this; the film theory asymptote would be here slightly below, but the difference is not much. And as the Hatta number becomes larger and larger, you have the fast reaction asymptote obtaining E is equal to root M. And depending on the value of the instantaneous enhancement factor, you have got braches coming out of this asymptote and these are increasing values of E infinity.

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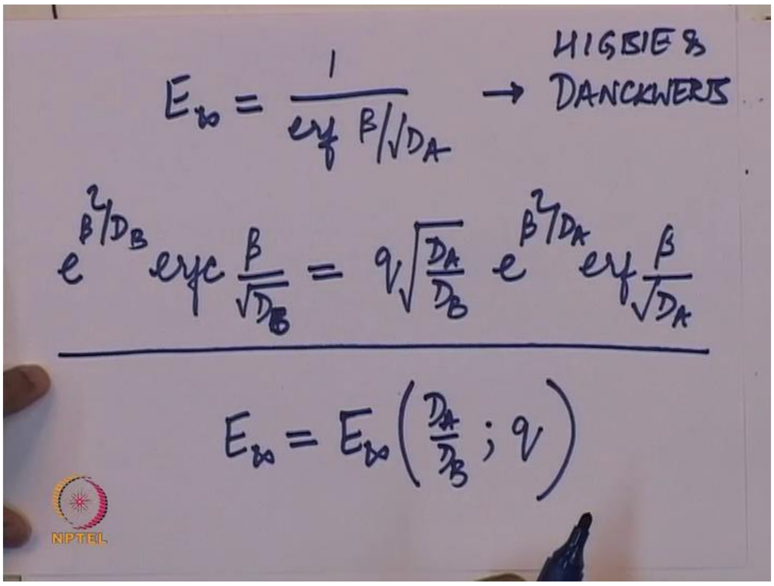

$$E_\infty = \frac{1}{\operatorname{erf} \beta/\sqrt{D_A}} \rightarrow \text{HIGBIE \& DANCKWERTS}$$

$$e^{\beta^2/D_B} \operatorname{erfc} \frac{\beta}{\sqrt{D_B}} = q\sqrt{\frac{D_A}{D_B}}\, e^{\beta^2/D_A} \operatorname{erf} \frac{\beta}{\sqrt{D_A}}$$

$$E_\infty = E_\infty\left(\frac{D_A}{D_B} ; q\right)$$

And the E infinity itself is given by normally by this expression here with beta being calculated by that expression.

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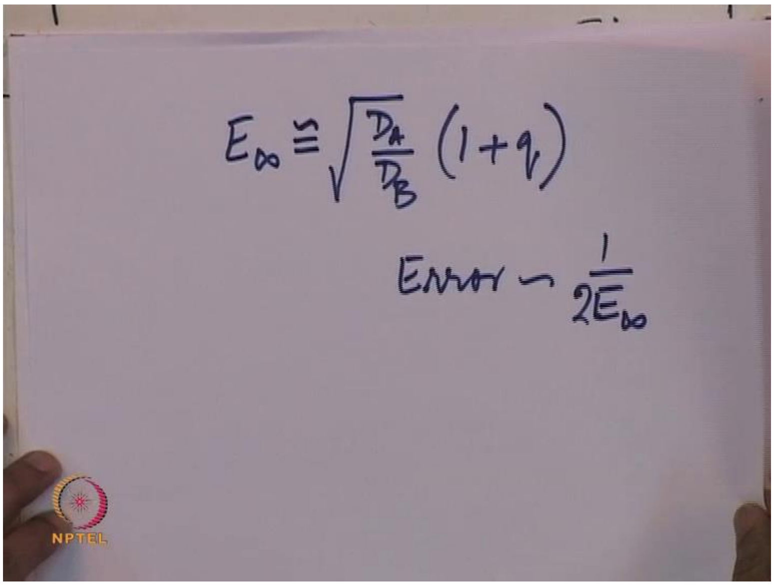

$$E_\infty \cong \sqrt{\frac{D_A}{D_B}}\,(1+q)$$

$$\text{Error} \sim \frac{1}{2E_\infty}$$

But for larger values of E infinity we can use this approximation.

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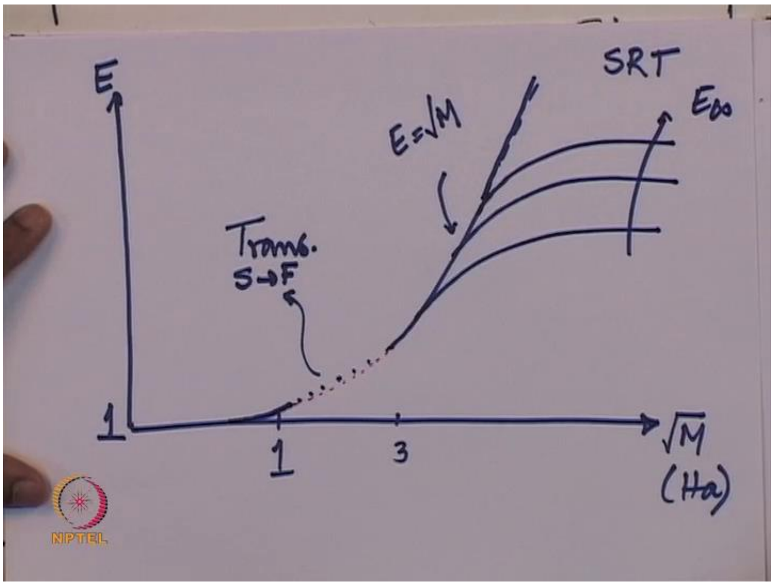

So, we have the slow reaction regime, where film theory is equal to the surface renewal theory is identical with the surface renewal theory. We have the transition regime, where to a good approximation, you can calculate the enhancement factor by either the expression given by the film theory or the expression given by the surface renewal theory. The 2 differ by a few percent at most.

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And then, in the fast reaction regime once again, you have got a situation where this surface renewal theory and the film theory agree completely for reasons that we have elaborated on earlier. And then in the instantaneous reaction regime there is a difference, if the diffusivities of A and B are very different from each other. So, there is this region what we have normally called as the transition fast to instantaneous, so this regime. So, before this regime we have the fast reaction regime E is equal to root M. And beyond this we have got the instantaneous reaction regime E is equal to infinity.

So, how do we calculate the enhancement factor in this region? 1 can of course, graphically do an interpolation between this asymptote and the appropriate asymptote here. But it has been shown that a good approximation is, to use the same expression that you derived with the film theory, using making a that is making a pseudo 1st order rate assumption, except that that a pseudo first order rate constant has is calculated as k c a b i using, the value of the concentration of B at the interface rather than, as k c b b chooses the concentration of B in the bulk.

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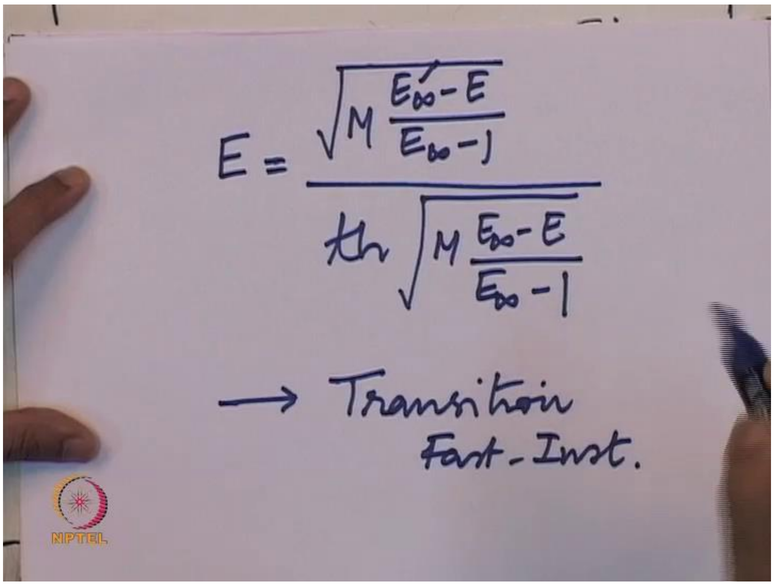

$$E = \frac{\sqrt{M \frac{E_\infty - E}{E_\infty - 1}}}{th \sqrt{M \frac{E_\infty - E}{E_\infty - 1}}}$$

→ Transition
Fast-Inst.

So, the expression that we had derived then, if you recall is; square root of M E infinity minus E divided by E infinity minus 1 divided by tan h of the same quantity M E infinity minus E divided by E infinity minus 1. So, this equation obtains for the transition regime fast to instantaneous. So, the only difference between the way you calculate enhancement factor in the surface renewal theory and the way you do it an film theory is that, while you are doing using the same expression, the value of E infinity that you use comes from penetration or the surface renewal theory expression, which is different has we have seen, when the diffusivities are different as compared to the film theory situation.

So, the value of I mean the definition of E infinity so what is changes in this expression depending on what theory you use. So, we have completed the discussion of the various reaction regimes in both the film theory and the surface renewal theory. And an important point that it makes the entire discussion makes is that, while the film theory is supposed to be less accurate as compared to the surface renewal theory, in so far as the prediction of the mass transfer coefficient on the diffusivity is more correct in the surface renewal theories. When it comes to predicting the effect of reaction on the mass transfer rate in the slow reaction regime in the transition slow to fast to a good approximation and certainly in the fast reaction regime, that is, in the entire pseudo 1st order a situation; the film theory is nearly as good as the surface renewal theories, for the purposes of predicting the enhancement factor.

So, this is convenient because, in more complex cases it is always simpler to use the film theory because, there are ordinary differential equations and finite field and so on, as compared to the surface renewal theories. The only the places where there is the difference is, where the concentration of B starts to make a difference to the overall absorption rate, that is in the second order regimes.

So, having come so far now, let us see whether, we can relax some of the assumptions that we made at the very beginning. There are 2 important assumptions that we made. Number 1 was that there was no gas phase resistance and number 2 that, the reaction is second order that, is first order with respect to A and first order with respect to B. So, taking the first, taking the second assumption first, that is let us look at the effect of different reaction orders.

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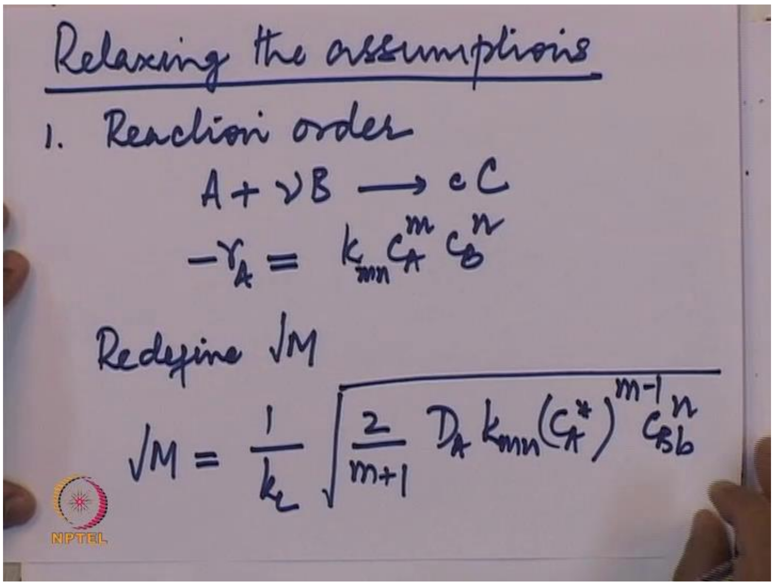

Relaxing the assumptions

1. Reaction order

$$A + \nu B \longrightarrow cC$$

$$-r_A = k_{mn} C_A^m C_B^n$$

Redefine $\sqrt{M}$

$$\sqrt{M} = \frac{1}{k_L}\sqrt{\frac{2}{m+1} D_A k_{mn} (C_A^*)^{m-1} C_{Bb}^n}$$

So, we will see the effect of relaxing the assumption. So, the first assumption is that, the assumption of reaction order. So, we have assume that A plus nu B going to c C is the reaction. And we have assume that, the rate, the intrinsic rate of this expression of this reaction is given by k c A c B; that is the case for which we have developed the theory so far. Suppose in the reaction is m’th order in A and n’th order in B and the rate constant is appropriately designate as k m n, what difference does this make and how good are theories that we have developed so far for the second order reaction in cases such as this.

So, it turns out that, all that needs to be done is; to redefine the Hatta number in the following manner. So, it is the physical mass transfer coefficient in the denominator. And 2 divided by m plus 1 diffusivity of A the rate constant C A star raise to the power m minus 1 C B bulk raise to the power n. So, provided you calculate your root M in that manner, this root M can be plugged into all expressions of the enhancement factor, that we have derived and you get reasonable results.

So, this is a very good way of extending the theory to reactions of other than second order. The second assumption that we want to examine, is assumption of negligible gas phase resistance.

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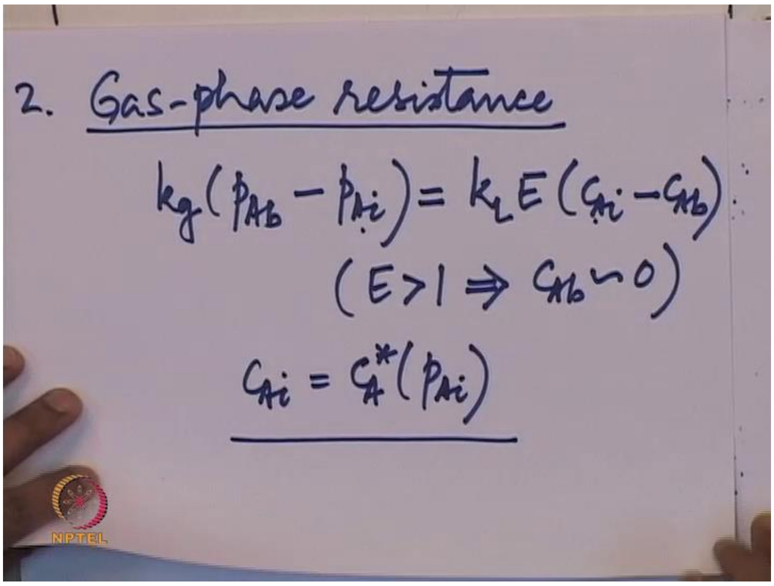

2. Gas-phase resistance

$$k_g(p_{Ab} - p_{Ai}) = k_L E (C_{Ai} - C_{Ab})$$

$$(E > 1 \Rightarrow C_{Ab} \sim 0)$$

$$C_{Ai} = C_A^*(p_{Ai})$$

And this turns out a quite simple if the gas phase resistance is not negligible. All that it means is that, the value of C A star that we have been using in the theoretical expressions; has now to be calculated as being in equilibrium, with the interfacial partial pressure of the gas, which in this case would be different from the bulk partial pressure of the gas.

So, we do that by, we calculate the interfacial partial pressure, by equating the flux of the gaseous solute from the gas site to the flux on the liquid site. In other words, we you we use the usual balance for 2 phase mass transfer, if p stands for the partial pressure of A and p A b is the partial pressure of A in the bulk of the gas, that is in the interior of the bubble if you like. And p A i is the value of the partial pressure at the gas liquid interface.

Then this would be equal to the rate at which the gases take an away. And that is k L into C A i minus C A b, where C A is the concentrate C A i is the concentration of A in the liquid at the gas liquid interface minus C A bulk is the concentration of a in the bulk. And usually as we have seen, if the enhancement factor needs to be considered in a E is greater than 1, it usually implies that C A b is close to C A.

So, either you have a situation where the rate is given by k L into C A i minus C A b or you have a situation where it is given by k L into E into C A i, C A b being equal to 0. And the C i and p A i are in equilibrium with each other, being the concentrations the partial pressure and the concentration on the 2 sites of the interface. Or we can write C A i is the C A star corresponding to p A i. And this could be given by Henry’s law or whatever, a suitable thermodynamic expression.

Therefore, the essential theory remains the same, except that, wherever you have had C A star being calculated as being in equilibrium with the bulk partial pressure of the gas, we replace that by the a quantity that is calculated as being in equilibrium, with the partial pressure at the interface, which itself is given by this expression here. So, that is all that needs to be done, in order to take gas phase resistance into account. In order to see how these things work, let us take an example.

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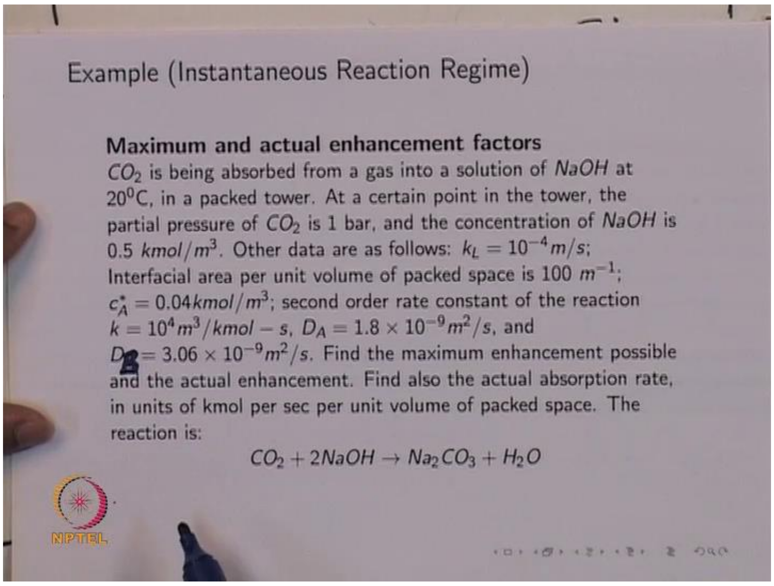

Example (Instantaneous Reaction Regime)

Maximum and actual enhancement factors

CO_2 is being absorbed from a gas into a solution of $NaOH$ at 20^0C, in a packed tower. At a certain point in the tower, the partial pressure of CO_2 is 1 bar, and the concentration of $NaOH$ is 0.5 $kmol/m^3$. Other data are as follows: $k_L = 10^{-4} m/s$; Interfacial area per unit volume of packed space is 100 m^{-1}; $c_A^* = 0.04 kmol/m^3$; second order rate constant of the reaction $k = 10^4 m^3/kmol - s$, $D_A = 1.8 \times 10^{-9} m^2/s$, and $D_B = 3.06 \times 10^{-9} m^2/s$. Find the maximum enhancement possible and the actual enhancement. Find also the actual absorption rate, in units of kmol per sec per unit volume of packed space. The reaction is:

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$$

So, we look at this example here for the instantaneous reaction regime and the transition to the instantaneous reaction. So, the example is out the calculation of the maximum enhancement factor and the actual enhancement factor. So, let me read the problem. Carbon dioxide is being absorbed from a gas into a solution of sodium hydroxide at 20 degree centigrade in a packed tower. At a certain point in the tower, the partial pressure of carbon dioxide is 1 bar, and the concentration of sodium hydroxide is 0.5 kilo moles per meter cubed. Other data are as follows.

The physical mass transfer coefficient is 10 to the power minus 4 meters per second. Interfacial area per unit volume of packed space is 100 meter inverse; that is 100 meters square per meter cubed of packed space. The concentration of A at the interface is given as 0.04 kilo moles per meter cubed. We assume that the gas phase resistance is negligible. The second order rate constant of the reaction is 10 to the power 4 meter cubed per kilo meter mole second. And the diffusivity of A and B are; this should be diffusivity of B, A and B are given. Find the maximum enhancement possible and the actual enhancement and find also the actual absorption rate in units of kilo moles per 2nd per unit volume of packed space.

So, the reaction stoichiometry is given here. So, 1 mole of carbon dioxide reacts with 2 moles of sodium hydroxide. So, how do we attempt this example? The maximum enhancement factor, we note first of all that the diffusivities of A and B are quite different from each other.

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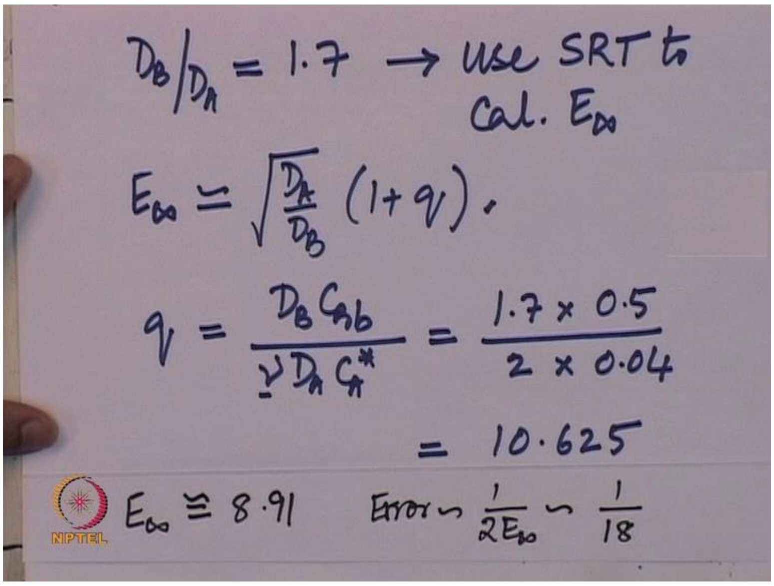

$D_B/D_A = 1.7 \rightarrow$ use SRT to Cal. E_∞

$$E_\infty \simeq \sqrt{\frac{D_A}{D_B}}\,(1+q).$$

$$q = \frac{D_B C_{Bb}}{\underline{\nu} D_A C_A^*} = \frac{1.7 \times 0.5}{2 \times 0.04}$$

$$= 10.625$$

$E_\infty \cong 8.91$ Error $\sim \frac{1}{2E_\infty} \sim \frac{1}{18}$

In fact, the ratio of the diffusivity of B to the diffusivity of A in this case turns out to be 1.7 if, you calculate this ratio from the given values of the diffusivities. Therefore, because this is significantly different from 1, we have to use the surface renewal theories, in order to calculate the maximum enhancement factor. And rather than use that complex expression, we will 1st see whether E infinity can be calculated by the approximate expression that we had, which is square root of D A upon D B 1 plus q, q itself is given by D B C B B divided by nu D A C A star. And putting in the values D B D B upon D A is 1.7 and C B B is 0.5 kilo moles per meter cubed nu the psychometric factor is 2 moles of NAOH per mole of carbon dioxide multiplied by c star that is 0.04.

This value turns out to be 10.625. Not a particularly larger number in this case, we have said that q is often of the order of a 100 or more, but carbon dioxide has a relatively larger solubility has compared to gases such as oxygen hydrogen etcetera. So, this value is a moderate value of about 10 or 11. If we substitute this value of q in the expression for E infinity above, we calculate the value of E infinity as 8.91. So, remember that, this is an approximate values since we have use this expression.

If you want to estimate the error, we can do this has 1 over 2 E infinity. And so approximately the error is going to be of the order of 1 over 18 or there about. So, that is an acceptable value of the error because, often the errors in the mass transfer coefficient itself are of a larger magnitude than this. So, let us proceed further and calculate the actual enhancement factor as the problem requires to do.

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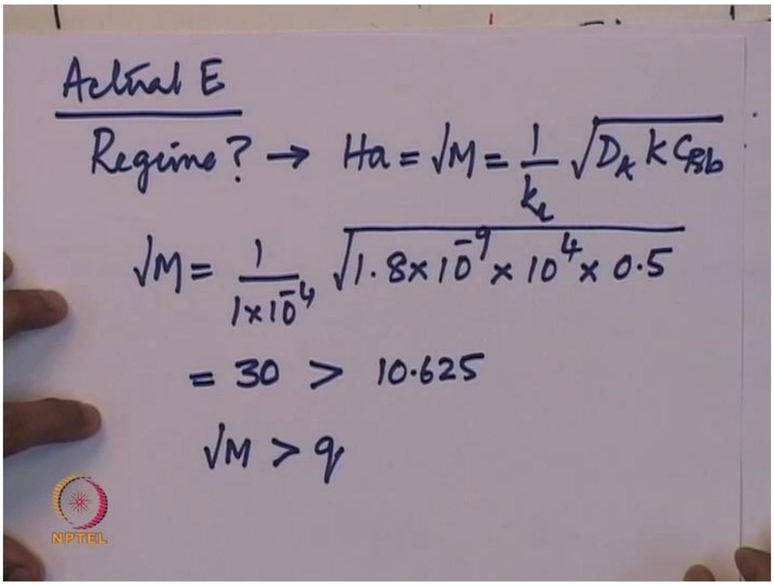

Actual E

Regime? → $Ha = \sqrt{M} = \frac{1}{k_L}\sqrt{D_A k C_{Bb}}$

$\sqrt{M} = \frac{1}{1\times10^{-4}}\sqrt{1.8\times10^{-9}\times10^{4}\times0.5}$

$= 30 > 10.625$

$\sqrt{M} > q$

So, in order to calculate the actual enhancement factor, we need to first estimate the regime, so that we know which expression to use. So, this question can be answered by calculating the value of the Hatta number or root M, which for a second order reaction can be calculated in the following manner. This is the standard definition for a second order reaction. And if you plug in the values turns out that 1 over M is 1 over k L which is 10 to the power minus 4 meters per second. All units are in SI. Therefore, we do not have to do any conversions. 1.8 multiplied by 10 raise to minus 9 is the value of diffusivity in square meters per second, k is 10 to the power 4 second order rate constant multiplied by 0.5 is the value of the sodium hydroxide concentration. So, gives your value of 30.

Now, so comparing this with the value of q, we find that this is greater than 10.625. So, we have the situation root M greater than q. Now, in order to assume instantaneous reaction, we would require that root M be far greater than q, while 30 is more than 10.625, is the difference large enough that we can assume instantaneous reaction. So, we are not sure of that.

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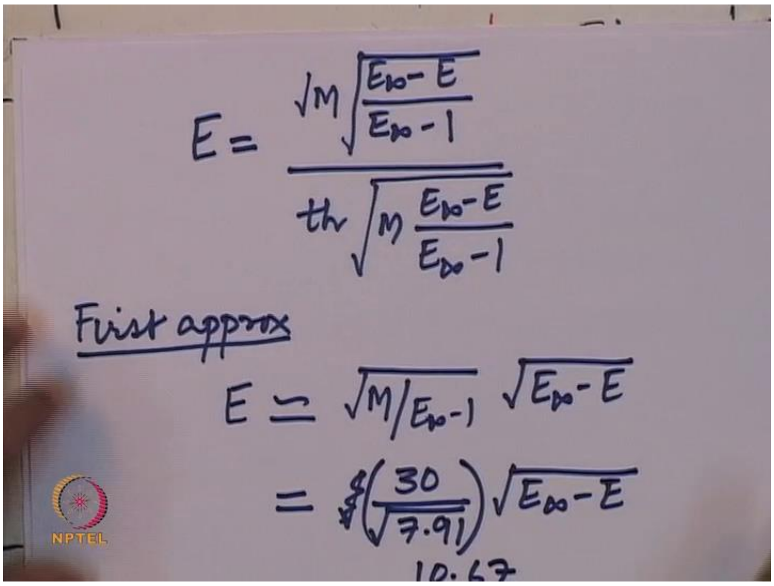

$$E = \frac{\sqrt{M}\sqrt{\frac{E_\infty - E}{E_\infty - 1}}}{th\sqrt{M\frac{E_\infty - E}{E_\infty - 1}}}$$

First approx

$$E \simeq \sqrt{M/E_\infty - 1}\,\sqrt{E_\infty - E}$$

$$= \cancel{\sqrt{\ }}\left(\frac{30}{\sqrt{7.91}}\right)\sqrt{E_\infty - E}$$

10.67

Therefore, let us know not assume that E is equal to E infinity and proceed to calculate the value of E using the transition regime expression, which is this here; square root of M into E infinity minus E divided by E infinity minus 1, this also under the square root divided by tan h of the same quantity right. In order to simplify our calculation and in order to put in place an iterative scheme for calculating the value of enhancement factor, we will calculate a first approximation as E is equal to the numerator. In other words, we assume that the value of this modified Hatta number if you like, M times E infinity minus E divided by E infinity minus 1 is large enough, that is, it is larger than the 3, so that we can assume the hyperbolic tangent of this quantity to be nearly equal to 1.

So, if you do that then, we can calculate the first approximation as root M divided by E infinity minus 1 into square root of E infinity minus E, where I have just separated out the values that we know from the value that we do not know. So, this is square root of well square of M, we note be 30 divided by square root of E infinity is 8.91, so we have 7.91 here multiplied by E infinity minus E under the square root. And this gives you a value of this number here turns out to be 10.67.

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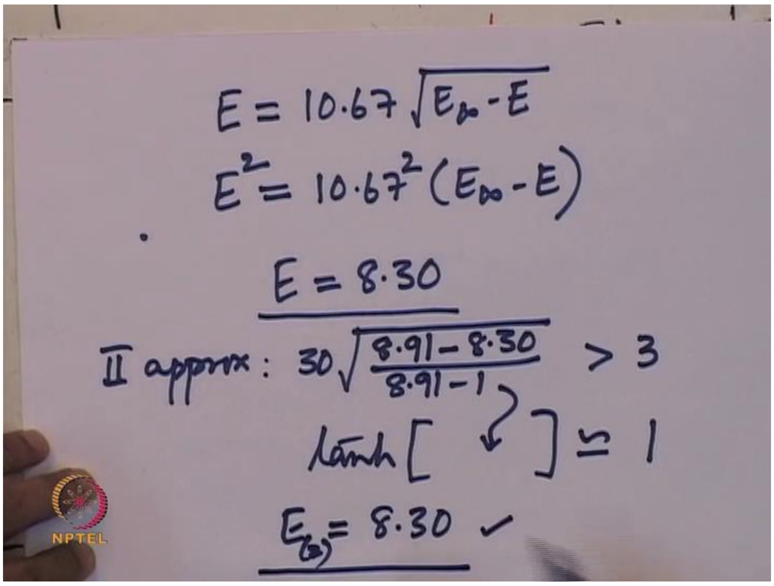

$$E = 10.67\sqrt{E_\infty - E}$$

$$E^2 = 10.67^2(E_\infty - E)$$

$$\underline{E = 8.30}$$

$$\text{II approx} : 30\sqrt{\frac{8.91 - 8.30}{8.91 - 1}} > 3$$

$$\tanh[\quad] \simeq 1$$

$$\underline{E_{(2)} = 8.30} \checkmark$$

And therefore, we have the equation E equals 10.67 times, square root of E infinity minus E. And E infinity we note be 8.91. So, we a can square this and obtain the value of E as from this quadratic expression 10.67 squared into E infinity minus E. This is the standard quadratic equation which we can solve. And this will give you a value of E as 8.30 which is not too far from 8.91, which is the value that we had estimated for the instantaneous enhancement, that is the maximum value of the enhancement factor.

So, what we are saying is that, even for root M, a factor of 3 higher than q, the reaction is almost totally in the diffusion control regime that is in the instantaneous reaction regime. So, now, since we made the approximation of the denominator; that is the hyperbolic tangent term in the denominator being equal to 1, we can test out that assumption by the calculating the second approximation, where we calculate this quantity square root of M which is 30, square root of M is 30 E infinity minus 1 E infinity minus E divided by E infinity minus 1.

So, this turns out to be a value that is sufficiently large that, this is greater than 3. Therefore, the tan h of this quantity here is approximately equal to 1. So, the second approximation also turns out to be 8.30. So, we have conversion a value of the enhancement factor as 8.30, we accept that value. And now, we are ready to calculate the absorption rate.

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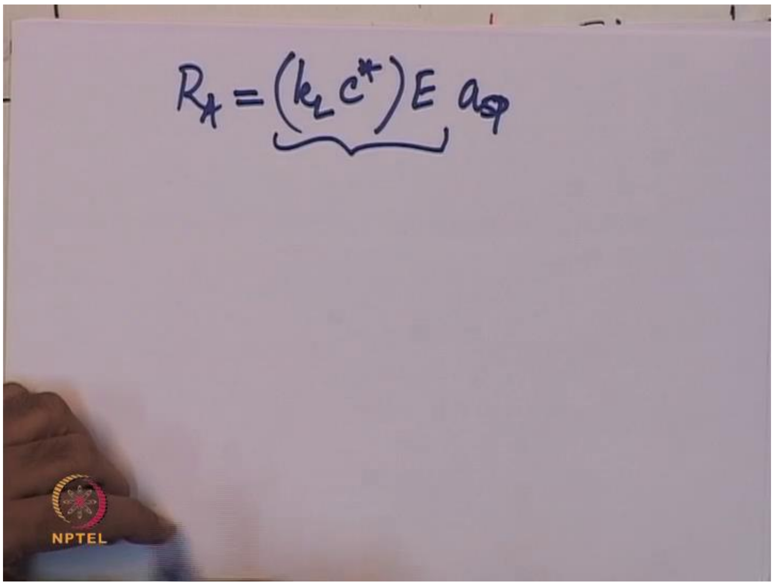

$$R_A = \underbrace{(k_L c^*) E}\, a_{sp}$$

So, we do that in the following manner. Absorption rate is the absorption flux, that is, k L c star which is physical absorption flux multiplied by the actual enhancement factor. This is the chemical absorption flux actual absorption flux. But we want the rate in units of moles per centimeter cubed of packed space per second. Therefore, we can multiply this by the interfacial area a s p which is these square meters of area available per unit volume of packed space.

So, if we … we can substitute this and calculate the value, I will leave that to you. 1 point that we should note is that, in our consideration of the various regimes and calculation of rates and so on, we have come across several definitions of this quantity, which we have called the interfacial area. So, in our theoretical development, we used a hat which we called as the interfacial area per unit volume of liquid. In 1 of the earlier examples, we had the case of a sparged reactor, in which the term interfacial area per unit volume of dispersion was introduced.

Now remember that the volume of dispersion includes the volume of liquid and the volume of the held up gas. So, this quantity of the, this definition of the interfacial area is little different from the interfacial area a hat that we have used in the theoretical development. And this example, we have encounter the interfacial area per unit volume of packed space.

So, basically it does not make a difference to your calculation of the flux at all because, that is given by this expression here. Depending on what units you want the rate to be in, you have to multiply this by the appropriate type of interfacial area per unit volume. So, here the rate is required in moles per unit volume of packed space per second. So, use the interfacial area has square meters per meter cubed of packed space. So, that is matter that is fairly trivial and does not need to engage our attention in any further.

So, now, this is the rate expression that you would use in the design of we fact bit reactor itself. In other words in any design exercise, you would do mass balance on the flowing face for a continuous equipment such as this, in which you say that if the equipment is operating at steady state, you would say that in any slice of the liquid, in slice of the packed bed, there is a certain amount of solute that is entering and there is certain amount of solute that is leaving. And the balance is being absorbed within that slice of the packed bit.

So, the absorption rate would be the rate of absorption per unit volume of the packed space multiplied by the volume of the slice. So, this rate of absorption per unit volume of the packed space is what we have calculated here. So, is the local rate expression that would go into any of your macroscopic balances or rector level balances. So, that completes our discussion of the gas liquid reactions. So, let us summarize what have seen in the past 6 or 7 lectures.

So, we have seen, we started by looking at how does mass transfer occur from a gas to an agitated liquid. And we considered this in terms of 2 possible mechanisms; 1 is the steady state mechanism what we called as the film theory, which is assumes that the entire resistance to gas liquid gas liquid mass transfer is located in a thin film of thickness delta, located at the gas liquid interface. Outside of delta the liquid is an a state of continuous mixing and because of the hydrodynamic forces, there. And because of that the concentration is uniform in that region.

So, there is a concentration various that goes from C A star to the bulk concentration that is prevalent in the rest of the liquid. And this concentration drop, occurs entirely in the a diffusion film. So, that is the assumption on which the film theory is built. And further we sad that, because this film is expected to be very, very small and we by later on with reference to the available values of the mass transfer coefficient, we estimated the volume of liquid in this film, to about the 0.1 percent or so of the total volume of the liquid.

So, because the volume contained in this film is so small in treating this film to be always in a state of steady state. In other words, any changes either on the gas site in terms of the changing partial pressure or on the liquid site in terms of the changing values of C A b, the film is able to immediately adjust on instantaneous bases to these changes. Therefore, the diffusing solute always proceed as though the conditions to over study.

So, we have a very simple equation to solve, the steady states diffusion equation which is the second order ordinary differential equation, with constant boundary conditions. So, this theory predicts that, mass transfer coefficient is proportional to the linear power of the diffusivity. And then we considered an alternative mechanisms for the mass transfer of A from the gas site to the liquid site and this mechanism assume that, the action of turbulence is not to restrict the distance over which the concentration drop occurs as assume in the case of the film theory.

But it is to actually periodically throw elements of liquid from the bulk to the gas liquid interface. And depending on the nature of the hydrodynamic field, there is a certain time period during which, individual a elements of liquid stay at the gas liquid interface and then leave. Because this time periods are expected to be short, the in general the processes assume to be of an unsteady state nature. So, here that is number 1 and the second thing that happens is that, because the time of exposure is small, the depth of penetration is also small and therefore, the surface element can be assumed to be infinitely thick from point of view of the diffusing solute.

So, we get to solve a partial differential equation for the second order first order in time and 2nd order in distance, in order to calculate the absorption flux in a single surface element as a function of the time it has spent at the interface. In order to calculate the average of absorption rate at that location, we have to consider the unit gas liquid interface at that location, which itself is a mosaic of several surface elements of various surface ages.

So, the absorption rate in these different elements has to be average in order to get the overall absorption rate. And we can do this averaging by assuming 2 types of surface age functions or age distribution functions if you like. And these give rise 2 different theoretical pictures; 1 which was originally proposed by Higbie where is said that every element of liquids spent exactly the same amount of time at the gas liquid interface as a every other element.

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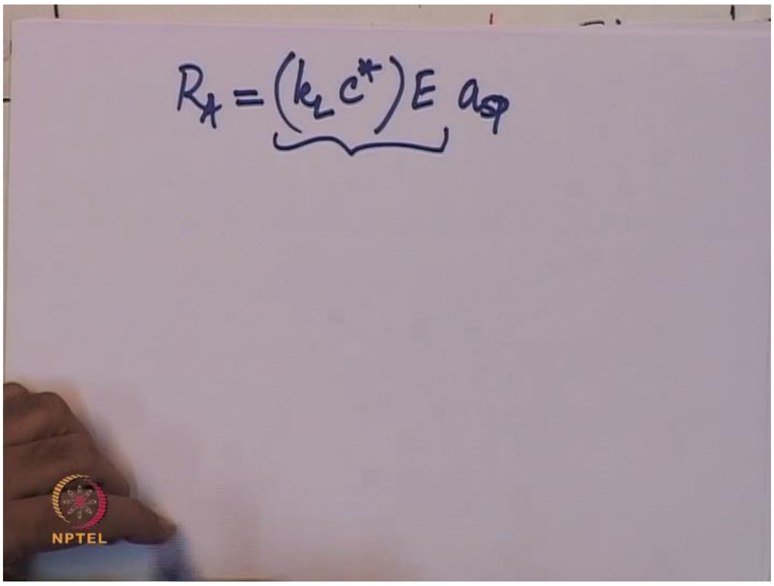

$$R_A = \underbrace{(k_L c^*) E}\, a_{sp}$$

And the second 1 due to Danckwerts who said that, the picture at the gas liquid interface is more like in well mixed to vessel, where elements of liquid are arriving randomly and departing randomly from the gas liquid interface. So, irrespective of which distribution function you use, it turns out that the a mass transfer coefficient is predicted to be predicted to have a square root dependence on the a diffusivity. And if you compare these predictions of the film theory and the surface renewal theory with the experimental data, it turns out that the surface renewal theories are closer to the actual picture than the film theory.

But irrespective of that, we should realize that neither of these theories is able to predict the physical mass transfer react at the any real sense because, each of these theories has a parameter, that usually in most realistic contacting situations, cannot be calculated from first principles. Therefore, the theories are in some sense useless in their ability to predict mass transfer rate is concerned.

But the usefulness theories is in their ability to predict the effect of chemical reaction on the mass transfer rate, what is called as the enhancement factor. So, this is the business that we address next. And we saw that, whether you are a proponent of the film theory or whether you are a proponent of the surface renewal theories, the effect of chemical reaction on mass transfer, depends on a value of depends on the value of a parameter called as a Hatta number, which is the relative rate of reaction to the rate of diffusion.

So, this there is a definition of the Hatta number that arises the non dimensionalization of the relevant diffusion reaction equations. And as the Hatta number increases, the reactions are the reactions being considered or of ever increasing severity with respect to the mass transfer rate or the diffusion rate. So, we have the slow reaction regime and we have the fast reaction regime. And in between, we have the transition from slow to fast reaction. And all through this, there 3 regimes; the slow reaction, the transition and the fast reaction, the assumption of pseudo first order rate holds because, the value of the Hatta number or the value of M that is, the square of the Hatta number is much less than the relative abundance factor, which governs whether, concentration of B is going to be uniform write up to the interface or not.

So, in all of these regimes, it does not really matter as to whether, you use the film theory to calculate the enhancement factor or the surface renewal theories to calculate the enhancement factor. Fair enough there is a bit of a difference in the transition regime, but that difference is of the order of few percent. And if you consider the uncertainty is in the values of the physical mass transfer coefficient itself. So, this error is usually subsumed in the errors with which you can calculate the rate of a absorption overall.

So, the point is that, as long as you got a pseudo first order situation or as long as you have a situation in which the concentration of B does not play a role in the absorption rate expressions, the actual mechanism of mass transfer turns out to be important; the film theory and the surface renewal theory predict the much the same kind of values for the enhancement factor.

So, then for larger values of root M that is for reactions which are of even higher severity than the once set we have considered so far, the reaction is fast enough to deplete the concentrations of B close to the interface. And this is where the differences between the 2 sets of theories starts to surface. And here by enlarge; we should go with the more realistic theory that is, the surface renewal theory. Fortunately it turns out that, for most practical situations, the expressions from the surface renewal theories or not very different or not very difficult rather to evaluate the enhancement factors from. And therefore, we can uses surface renewal theories without too much difficulty.

So, these are the various ways in which we can calculate the enhancement factor. And once you have calculated the enhancement factor, the local rate of the absorption, at any point within the equipment, is given by the local mass transfer coefficient and multiplied by the driving force multiplied by the enhancement factor. So, you had the expression k L into C A star minus C A b for the physical mass transfer rate and all you got to do now is to put in this value F the enhancement factor as a multiplicate to this expression. Much as this we use the effectiveness factor in the case of gas solid reactions, to modify the intrinsic rate expression.

So, there, the basic case was the case of reaction and the effectiveness factor which had a value of less than 1 multiplied this intrinsic reaction rate give it to the actual reaction rate. Here the base case is the base of mass transfer and this has to be multiplied by an enhancement factor, which has a value greater than unity in order to give the actual rate of mass transfer.

So, once you know the actual rate of mass transfer rate, this is the rate expression that goes into various equipment level balances, which you use either for analysis of process equipment or for design process equipment. So, with that we have now completed setting up the recusant operators for doing an analysis or design of gas liquid reaction equipment, where the enhancement factor calculations have to precede the writing the expression for the local rate. So, we shall close this set of lectures here.

Thank you for your attention.