

Chemical Reactions Engineering II
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Lecture - 23

GLR-4: Fast reaction example; Instantaneous reaction regime

Welcome back. In our consideration of the effect of chemical reactions on mass transfer, we saw the slow reaction regime. And proceeding further, in the last lecture we got some idea of what the fast reaction regime is. And the fast reaction regime is if you recall; 1 in which the entire reaction gets completed within the film. So, between 0 and delta as you move away from the gas liquid interface, all the reaction is done and no solute, no unreacted solute passes into the bulk.

So, the bulk just serves as a an inventory of the reactant b. It supplies b to the locale of the reaction which is the film and also it stores the reaction product as it diffuses out of the a reaction zone. So, that is all that the a bulk of the liquid is being used for, all the reaction is being done, being carried out by the film, which has we have seen represents only 0.1 percent also of the total liquid volume.

Now, this fast reaction regime has some interesting applications in the characterization of mass transfer equipment or industrial contactors. And we will just spend a few minutes, looking at a how these applications arise.

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(FRR)

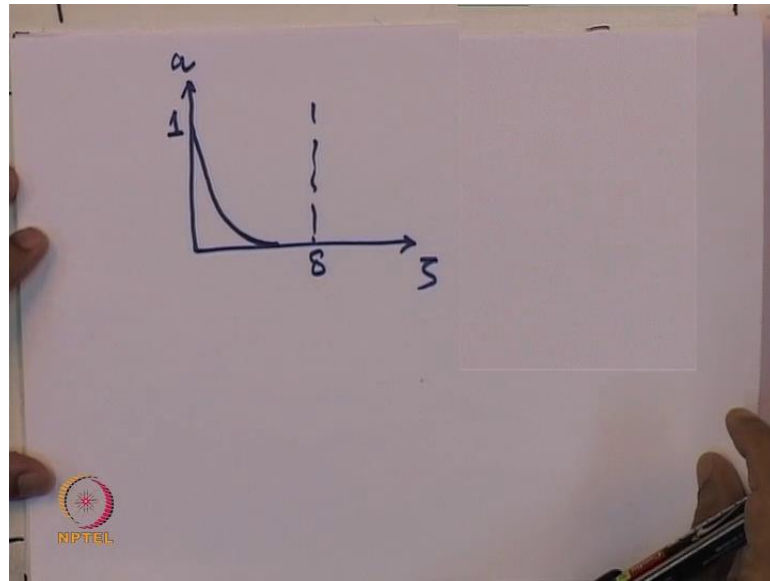
$$E = \sqrt{M} = \delta \sqrt{\frac{k C_B b}{D_A}}$$
$$E = \frac{1}{k_L} \sqrt{D_A k C_B b}$$
$$R_A = k_L \hat{a} C_A^* \cdot E = \hat{a} \sqrt{D_A k C_B b} C_A^*$$

If, you revisit the equation that we derived in the last lecture, for the enhancement factor for the fast reaction regime, enhancement factor was written as square root of M and this from the definition of root M , is δ square root of $k C_B b$ divided by D_A . Now recalling that, δ is itself D_A by k_L , we can write this as 1 over k_L square root of $D_A k C_B b$. So, this is the enhancement factor in the fast reaction regime, in terms of the physical mass transfer coefficient.

So, substituting this into the absorption rate expression which is nothing but $k_L a$ into C_A^* multiplied by the enhancement factor. So, this is the physical absorption rate and this accounts for the effect of chemical reaction. We see that, when we substitute for the enhancement factor from this expression, this k_L gets canceled out and we are left with this expression $k C_B b$ multiplied by C_A^* .

So, this is an interesting expression in the sense, that it shows that, there is an absorption that is going on and the absorption rate is independent of the mass transfer coefficient, is a very peculiar situation where you are got a mass transfer process that is going on, that is independent of the mass transfer coefficient.

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Now, if you think about it, the reason why this happens is content in the way concentration profiles work out in the fast reaction regime. And we have seen that, if you are plotting the concentration of a as a function of $zeta$. Then you have seen that, in general in the fast reaction regime here of profile, that something like this. In other words, the concentration profile extends to a distance that is well within δ , at the beginning of the fast reaction regime. In other words, for values of \sqrt{M} which have just sufficient to send the reaction into the fast reaction regime, this point is δ .

But for all larger values of \sqrt{M} or the Hatta number, the concentration profile extends to a distance that is much less than δ . What this means is that, the diffusing solute does not know where the film ends. In other words, the concentration profile does not get to see the end of the film. And therefore, the entire concentration profile as well as the absorption flux; these expressions become quite independent of δ . And since it is δ which brings in the mass transfer coefficient, the equations turn out to be independent of the mass transfer coefficient as well.

So, this is the interesting situation that arises, when the reaction is completed well within the film. And the implication of that, is that, there is here an opportunity for us. If you look at this expression; there is here an opportunity for us to calculate this quantity a interfacial area per unit volume of liquid, from experimental measurements of rate, knowing the rate constant and diffusivity and the solubility of the gas.

So, this is 1 of the uses to which fast reaction regime is often put in the characterization, of mass transfer equipment. And in order to see how this works, let us take an example; that will also serve to illustrate some of the aspects of fast reaction regime that we have talked about.

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Example (Fast Reaction Regime)

Part 1: Rate constant of an unknown reaction

An oxidation reaction $A + \nu B \rightarrow P$, which is first order in oxygen (A) is carried out in a stirred cell with a flat gas-liquid interface of 132 cm^2 at atmospheric pressure with pure oxygen. Over a stirrer speed range of 60 - 200 RPM, the rate of absorption was measured to be nearly constant at $1.23 \times 10^{-5} \text{ mol/s}$, as measured by the difference in the flow rates of gas at inlet and outlet; it was also independent of the volume of liquid in the vessel. The solubility of A in the liquid phase follows Henry's law with $H = 5.8 \times 10^{-7} \text{ mol/cm}^3/\text{atm}$. Find the rate constant of the reaction. ($D_A = 2.1 \times 10^{-5} \text{ cm}^2/\text{s}$; concentration of B = 0.01 mol/cm^3).

So, I have here an example. The example works in 2 parts. In the first part we try to calculate the rate constant of unknown reaction. So, we have an oxidation reaction A plus nu B going to P, where a is oxygen. And the reaction is given to be first order in oxygen. It is carried out in a stirred cell and we will see we will make use of the example; to illustrate some model gas liquid apparatus as well. So, while we start solving this equate this problem, we will see what stirred cells look like and so on.

So, the stirred cell essentially has a flat gas liquid interface. In other words, there are no bubbles going through the liquid, there is the liquid and on top of the liquid there is the gas and there is a flat gas liquid interface that separates the gas from the liquid. The area of the gas liquid interfaces given. And the whole operation is being carried out at atmospheric pressure and pure oxygen is being used. Over a stirrer speed range of 60 to 200 revolutions per minute, the rate of absorption was measured to be nearly constant, at $1.23 \times 10^{-5} \text{ mol/s}$. So, this is total rate, it is not the rate r_A that we have been talking about, which is rate per unit volume.

So, this is the rate in units of moles per second. So, how is this measured? This is simply measured by the difference in the flow rates of gas at inlet and outlet. You are sending a certain amount of gas; so many moles per second of gas are coming in. And so many moles of gas per second are going out. So, the difference is getting absorbed and that is the quantity that we are measuring.

The absorption rate was also independent of the volume of liquid in the vessel. The solubility of A in the liquid phase follows Henry's law. You recall Henry's law from your basic thermodynamics classes. Henry's law states that; for several gasses, mainly sparingly soluble gases, the concentration at equilibrium is directly proportional to the partial pressure and the proportionality constant is what is called as the Henry's law constant. And that, for this system, for the system oxygen dissolving in whatever liquid contains B is given by 5.8×10^{-7} moles per centimeter cube for atmosphere. Find the rate constant of the reaction given this information.

Some additional pieces of information are that the diffusivity is 2.1×10^{-5} centimeter square per second and the concentration of B is 0.01 moles per centimeter cubed. So, let us solve this part of the problem before going to the second part of the problem. So, first of all, let me spend a couple of minutes saying what stirred cell is.

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Gas in $\frac{\text{mol}}{\text{s}}$ → Gas out $\frac{\text{mol}}{\text{s}}$

Gas
Liq
STIRRED CELL

$$(R_A V_L) = 1.23 \times 10^{-5} \text{ mol/s}$$

$$C_A^* = H p_{O_2} = 5.8 \times 10^{-7} \text{ mol/cm}^3$$

$$D_A = 2.1 \times 10^{-5} \text{ cm}^2/\text{s}$$

REGIME? → $q = \frac{D_A C_A b}{v D_A C_A^*} \sim \frac{10^{-2}}{0(10^{-7})} \sim 0(10^5)$

A stirred cell is model piece of gas liquid contacting equipment, which is use to calculate the values of the rate constants of unknown reactions, such as the 1 we have right hand

now. So, it is; let us say it close to vessel, there is the liquid. And there is the gas and there is a stirrer, which just sweeps the interface. Without creating much or ripple or anything like that, it just goes to the round and round just stirring up the interface. So, the interface essentially remains flat. Therefore, the interfacial area that is available for gas liquid mass transfer, is the across section area of the vessel essentially.

So, this kind of apparatus can be operated in with a dead end flow of the gas. In other words, there is only an inlet and no outlet, as the gas is absorbed, more gas flows into the chamber. And the rate of inflow of the gas, gives directly the rate at which gasses being absorbed. But, in this particular case, we are told that, there is a gas inlet and there is a gas outlet. Optionally you could have a stirrer for the gas phases well, in order to keep the gas phase well mixed. And so this is gas in and this is gas out. And you can measure the molar flow rates of this; you know streams; that is gas coming in and gas going out. So, this is kind of equipment, in which the particular experiment that we are considering has been done.

Now, the advantage of this is; the interfacial area is exactly known. So, if you can conduct fast reaction in this kind of the equipment, since the interfacial area is known you can calculate the rate constant. So, we will see how that is done. What is given; so we will just tabulate the data that is given. So, what is actually given is total absorption rate, that is, the rate of the absorption in moles per centimeter cube per second multiplied by the liquid volume. So, that is what is given. So, this is 1.23×10^{-5} moles per second and what is C_A^* ? It is nothing but the Henry's law coefficient multiplied by the partial pressure of oxygen in this case.

Since, it is the experiments being conducted at atmospheric pressure and it is pure oxygen, p_{O_2} is 1 atmosphere. And therefore, C_A^* is given by the Henry's law coefficient itself in magnitude. The diffusivity is given as 2.1×10^{-5} centimeter square per second. The first thing is that, we have to sort out is what is the regime. And is it a regime that facilitates the calculation of the rate constant.

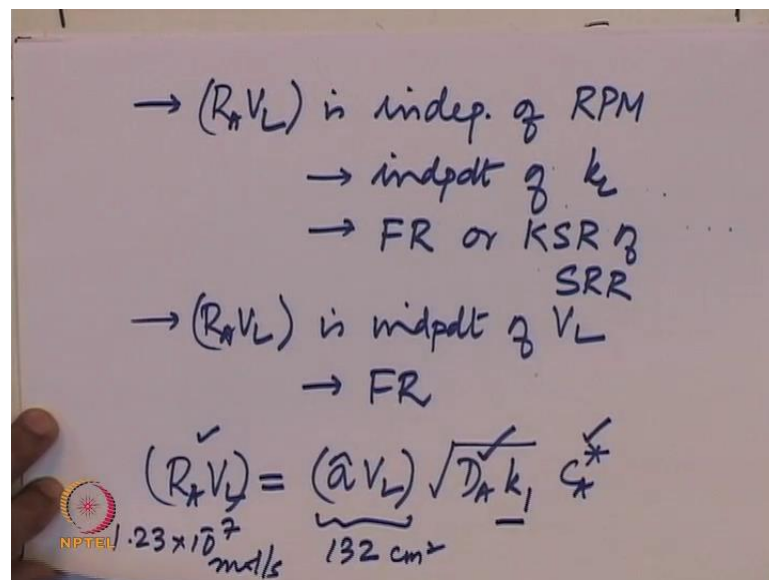
Now, we are told that, there are 2 pieces of information here. 1 is that, before we go to what the problem directly states, we note that, the reaction is given to be a first order reaction, that is what it says here. And it is clear from the concentration of B as to, why this would be a 1st order reaction even if there is a dependence of the rate on the

concentration of B. Because if you look at the value of q , q is going to be $D_B C_B b$ divided by $\nu_D A C_A^*$ and it is approximately going to be the ratio of $C_B b$ to C_A^* given that D_B and D_A are about equal and ν is a number like 1.

So, $C_B b$ is 10 to the power minus 2 and C_A^* is of the order of 10 to the power minus 7 . So, this is used number. So, q is order of 10 to the power 5 . So, this means that, even if the reaction were to have some order with respect to B; that is not going to be apparent in any experiment that is conducted under these conditions, because the concentration of B is not going to have a profile within the film.

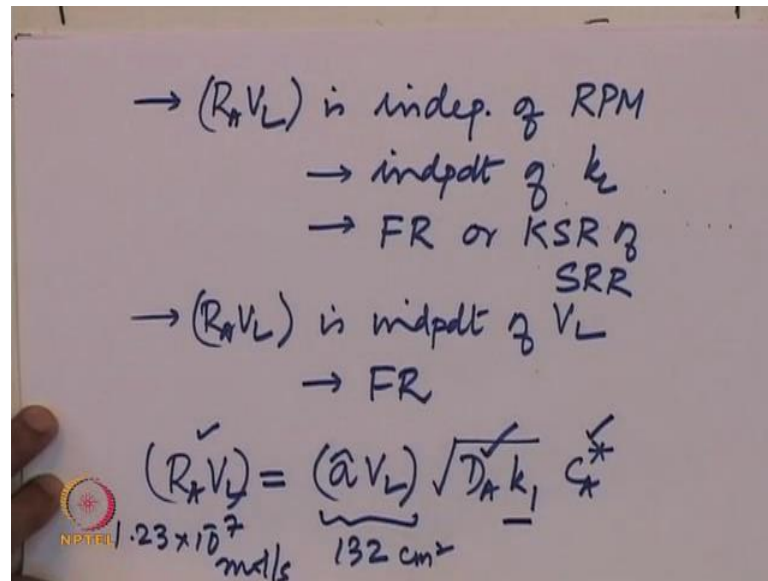
So, the pseudo first order assumption is confirmed. And in any case we did not have to do this, because the problem statement itself says that, the reaction is first order. What about is it in the slowest reaction regime, is it in the fast reaction regime, what is happening. So, for that we need to calculate; 1 way of doing that is to calculate the value of root M. But we do not have enough information to calculate the value of root M. In fact, the rate constant that figures in the definition of root M; is the objective of this whole exercise.

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On the other hand, it says that the, it is well known that in an equipment of this kind, the mass transfer coefficient is dependent on the stirrer speed. That is an essential characteristic of a stirred cell, by rotating stirrer faster you can increase the mass transfer coefficient.

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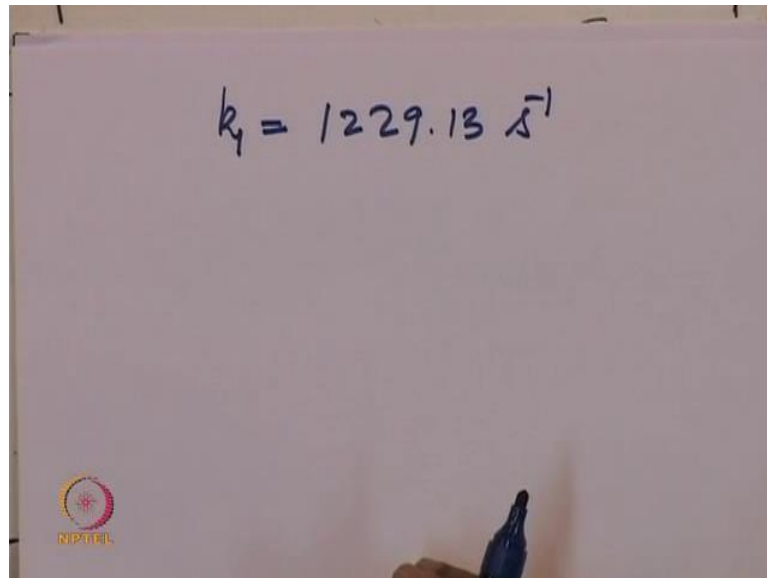
What the problem statements says is that $R_A V_L$ is independent of RPM. So, this means that it is independent of k_L . So, this suggests that, it could be fast reaction, but you should not forget that, there is another regime in which also the absorption rate would be independent of k_L and that is the kinetic sub regime of the slow reaction regime right. Just, because you see the rate independent of k_L , you cannot immediately jump to the conclusion that, you have the fast reaction regime. You should also consider the possibility that, we are under kinetic control within the slow reaction regime and the liquid is running saturated.

However, we note that if it was the kinetic sub regime then, the whole liquid within the vessel would be conducting the reaction. And therefore, if you vary the liquid volume in the vessel, keeping the gas liquid interfacial area the same, it would have an effect; it would have an proportional effect. So, if you double the volume, the total rate of absorption moles per second would also double. However, we have been given that $R_A V_L$ is independent also of the liquid volume. So, this is the statement that rules out kinetics sub regime or kinetic control under slow reaction regime.

So, we can now conclude that the reaction is in the fast reaction regime. So, therefore, we can write in a expression for $R_A V_L$ which is interfacial area times the liquid volume, that is, the total interfacial area that is present multiplied by square root of D_A . And $k_1 C_A^*$ is nothing but the first order rate constant multiplied by C_A^* . In this

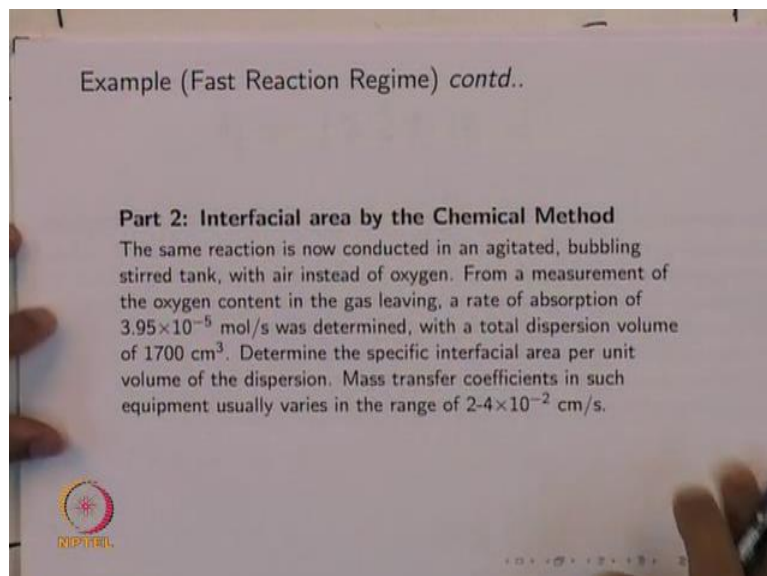
expression, we are given this to be 132 centimeter squared. This value is known, this value is known and it is given as 1.23 multiplied by 10 to the minus 7 mol per second. So, we should be able to C A star value is known. So, we should be able to find the value of k_1 .

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$$k_1 = 1229.13 \text{ s}^{-1}$$

If you plugged in the numbers, it turns out that the value k_1 is 1229.13 second in volts. So, it is indeed fairly large rate constant that you find there. So, that completes the first part of the problem. Now, let us look at what do we do with this.

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Example (Fast Reaction Regime) *contd.*

Part 2: Interfacial area by the Chemical Method

The same reaction is now conducted in an agitated, bubbling stirred tank, with air instead of oxygen. From a measurement of the oxygen content in the gas leaving, a rate of absorption of 3.95×10^{-5} mol/s was determined, with a total dispersion volume of 1700 cm³. Determine the specific interfacial area per unit volume of the dispersion. Mass transfer coefficients in such equipment usually varies in the range of $2-4 \times 10^{-2}$ cm/s.

The second part of the problem as seen here; involves calculation the interfacial area by the chemical method; obviously, would not be using the method to calculate the interfacial area in stirred cell, because the stirred cell interfacial area is exactly known. However, now that we have characterize the reaction in terms of its rate constant, we can take the same reaction, put it into another gas liquid contacting vessel, where the contacting pattern is more complicated, you are probably sparging the vessel with gas. So, there are bubbles running in zig zag direction, there is a certain gas hold up and so on.

So, there, the interfacial area is very uncertain and you can use the reaction which has now been well characterized to calculate the interfacial area, provided you can arrange a fast reaction regime in that vessel as well. So, let us see what the problem statement is. The same reaction is now conducted in an agitated bubbling stirred tank with air instead of oxygen. From a measurement of the oxygen content in gas, leaving a rate of absorption of 3.95×10^{-5} moles per second was determined, with a total dispersion volume of 1700 centimeter cubed.

So, what is being given is the dispersion volume, which means it is a total volume occupied by the gas a bubbles and the liquid. Determine the specific interfacial area per unit volume of the dispersion. Mass transfer coefficients in such equipment usually varies mass transfer coefficient in such equipment usually varies in the range offset 2 to 4×10^{-2} in units of centimeters per second.

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$k_g = 1229.13 \text{ s}^{-1}$

Part 2: FRR ? ←

Gas out
($P_{O_2} = 0.21 \text{ atm}$)

Gas in (Air)

$$C_A^* = H P_{O_2}$$
$$= 5.8 \times 10^{-7} \times 0.21$$
$$= 1.218 \times 10^{-7} \frac{\text{mol}}{\text{cm}^3}$$

So, once again, to address part 2, we should ask the question are we having the fast reaction regime in the new vessel that we have adopted for the second part of the problem. So, this is the vessel something like this and here you have got gas bubbles. So, the gases coming in here and gas is going out here. And this gas is air now, it is not oxygen. So, what is C_A^* ? C_A^* is nothing but once again H times partial pressure oxygen. And we shall assume that, the absorption is the overall flow rate of the gas is so large, that the partial pressure at the inlet and outlet all about the same. In other words, if there is a tremendous flow of oxygen coming in compare to the amount that is absorbed, almost all the oxygen is going out. And therefore, of course, nitrogen will go out, because it the liquid quickly gets saturated with nitrogen and thereafter there is no absorption time nitrogen.

Therefore, the gas out, has essentially the same composition as the gas in. If this is not the case, I would have to measure the partial pressure of oxygen in the outlet gas and makes some assumption that, the gas phases well mix. Therefore, the partial pressure everywhere inside the vessel is the same as at the outlet. Or you would, you may assume for example, that the gas is in plug flow, and therefore calculate a logarithmic average of the partial pressure between in inlet and outlet.

In order to avoid those complications and also the uncertainty about the residence timers, distribution whether it is well mixture plug flow or something in between, it is best to

conduct these kinds of the experiments, with a large flow rate of the gas such that, the partial pressures inside and outside at the inlet and outlet are the same. And if or some reasons, you cannot use that kind of high flow rate, then you could also employ a pure gas, in which case the partial pressure of oxygen is equal to the total pressure and once again there is no difference between inlet and outlet partial pressures.

Whatever is the case, in this case, we will assume that the outlet gas has a partial pressure of oxygen equal to that at the inlet which is 0.21 atmospheres. If that is the case, then we have the value of H: minus 7 and partial pressure of oxygen 0.21 and the value of this is 1.218 multiplied by 10 to the minus 7 moles per centimeter cubed, that is C A star. We still have at address this question of whether we have fast reaction regime.

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$$\sqrt{M} = \frac{1}{k_L} \sqrt{D_A k_1} \quad ? > 3$$

$$= \frac{1}{4 \times 10^{-2}} \sqrt{2.1 \times 10^{-5} \times 1229.13}$$

$$= 4.02 \quad \checkmark$$

$$(R_A V_L) = (a V_L) C_A^* \sqrt{D_A k_1}$$

3.95×10^5 ml/s

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In this case, the only where we can test that assumption is a to work out or estimate the value of root M. And this is 1 over k L square root of D A k 1 as we have shown in the first part of this lecture. And in order to see, so we want this, we are asking the question whether this is greater than 3. It is in all likely hood much less than q, because q has a used magnitude, but this is the 1 that we are interested in. Which means to say; I should calculate a minimum value of M based on the range of k L that is provided. And if that if that even the minimum value of root M is more than 3, certainly we can be assured that, root M falls in the range of fast reaction regime.

So, we should assume the largest value of the mass transfer coefficient within the range that is provided, multiplied by square root of $D A$ which is 2.1×10^{-5} multiplied by, now we know the value of k_1 which is 1229.13 s^{-1} and this turns out if you work out the numbers, to a value of 4.02 . So, this is satisfactory, it is on the one hand greater than 3 . On the other hand, it is much less than q . Therefore, the conditions of fast reaction regime are fully filled.

So, we can once again apply the same equation $R A V_L$ equals $a V_L C A^*$. This is multiplied by $D A k_1$, which is the expression for the rate of the absorption in the fast reaction regime. Now we know this, this is given to the value of this was given to be $3.95 \times 10^{-5} \text{ moles per second}$, this is what is unknown here, $C A^*$ we have just calculated, $D A$ and k_1 are now known, k_1 is known from the 1st part of the problem.

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Handwritten calculations on a whiteboard:

$$\hat{a} V_L = \text{Total Interfacial Area} \\ \text{cm}^2 \\ = 2018.56 \text{ cm}^2$$

$$\left. \begin{array}{l} \text{Int. area} \\ \text{Per unit} \\ \text{Vol of} \\ \text{dispersion} \end{array} \right\} = \frac{2018.56 \text{ cm}^2}{1700 \text{ cm}^3} \\ = 1.19 \text{ cm}^2/\text{cm}^3$$

'CHEMICAL' METHOD

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So, if substituted those numbers, we come up with a value for this \hat{a} which is the total interfacial area in centimeter squared. And this comes out to be 2018.56 centimeter squared. Now what is required is; interfacial area per unit volume of dispersion. This is what that we defined is; the interfacial area per unit volume of liquid, which is a different from the unit volume of dispersion, because the dispersion contains liquid as well as gas.

So, in this particular case, since the total interfacial area is known and the volume of dispersion is known given as 1700 centimeter cubed, we come up with the required

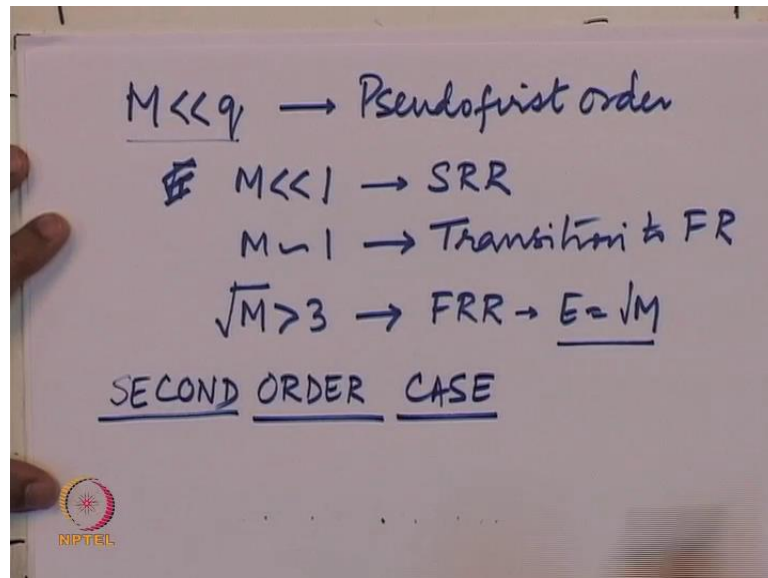
quantity is 1.19 centimeter squared per centimeter cubed or 119 meter square per meter cubed. So, this example illustrates; number 1: the kind of modulate equipment that are useful in using the using model reaction 2 characterize mass transfer equipment.

So, we identify a reaction which is which has a rate constant in the right ball park, that we suspect will be useful and which will operator as given contactors in the fast reaction regime. And we take this reaction whose rate constant is initially not known and conducted in a conduct it in situation, where the gas liquid interfacial area is given by the cross section of the vessel.

There are other module pieces are equipment which are also useful in calculating the value of the rate constant. We have illustrated 1 such a piece of equipment here which is stirred cell. You can conduct fairly simple experiments there and calculate the value of the rate constant. Then you take the value of rate constant and conduct the reaction in a in your equipment of interest, where the gas liquid dispersion might be far more complex, you might be bubbling the gas through and you might be agitating the whole gas liquid dispersion and so on. And you measure the rate once again and from the measures rates, you know the rate constant, you can calculate the interfacial area. So, this is what is known as the chemical method for measuring the interfacial area.

So, this is called as the chemical method of measuring interfacial areas. So, this is to be contrasted with physical methods, which for example, depend on such physical phenomena as lights scattering and so on or scattering of sound, various techniques are available. So, these will actually you know employ a physical means to measure the gas liquid interfacial area that is available. And in contrast those methods; it is this is called as the chemical method for measuring interfacial areas. And the chemical method is far more easier to employ and far more inexpensive to employ. Therefore, it has to be used in the contacting in the characterization of gas liquid contacting equipment for number of the decades. Let us proceed further in our consideration of reactions of increasing velocity. So, let us see where we are.

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So, we started by saying that our M is far less than q and this was the requirement for considering the reaction to be a pseudo first order. And with this we started by saying that, let us start with M which are value of M which are much less than 1 this k was the slow reaction regime. And then we went to values of M which are of the order of 1, this gave us the transition to fast reaction. And then, values of M exceed 3 then, you have the fast reaction regime.

So, if you consider reactions with higher and higher values of M , the equation E equals this is root M greater than 3, E equals root M will apply and the enhancement will go on increasing. So, as you consider values of root M that are progressively higher and higher, there will come a time, when this condition is no longer valid, for a given system which has certain value of q .

So, as the value of M increases, at some point this condition will be will start to get violated. M will have a comparable magnitude as compare to q . And if you increase further and will even go beyond the value of q . So, we will consider those kinds of reactions now. And really, because M is no longer much less than q , the concentration profile of B within the film cannot be ignored and the second order nature of the reaction will have to be consider. So, this is the case of second order.

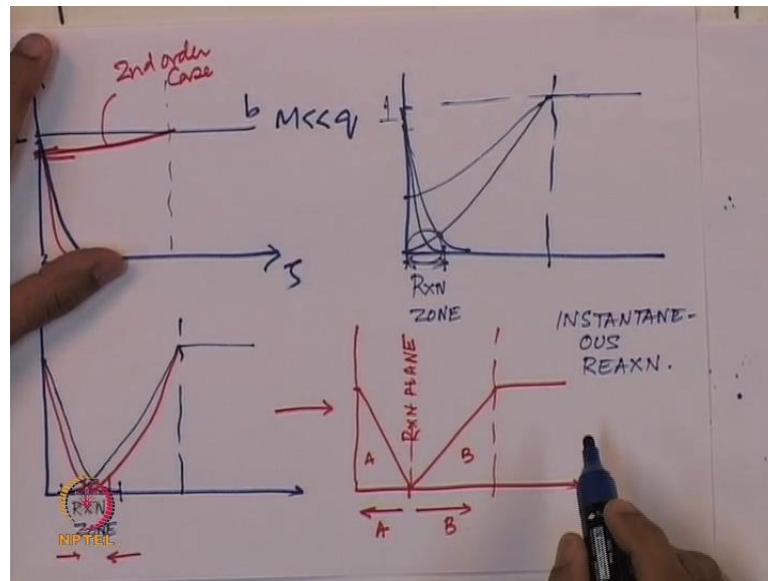
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$$\frac{d^2 a}{dz^2} = M a b$$
$$\frac{d^2 a}{dz^2} = \frac{M}{q} a b$$
$$z = 0 \quad a = 1 \quad \frac{db}{dz} = 0$$
$$z = 1 \quad a = 0 \quad b = 1$$

Recalling our original set of equations that we had, the governing equations in this case would be writing in terms of non dimensional variables, it was $d^2 a$ upon $d z^2$ equals $M a b$ and $d^2 a$ upon $d z^2$ equals M upon q $a b$. And the conditions are at $z = 0$ you have $a = 1$ and $\frac{db}{dz} = 0$ and at $z = 1$ you have $a = 0$ and $b = 1$.

So, we are now started using safely the condition that, there is no a in the bulk, but even because even by the fast reaction regime, there is no a even reaching the bulk of the liquid. So, this condition is the appropriate 1 to use for any reaction that is faster than those which are considering taking place and entirely within the film. So, now, this set of equations is a difficult animal to solve, because it is a second order coupled set of ordinary 2 ordinary differential equations. However, we need not solve this equation, because we can qualitatively consider in terms of our analytical process, as to what happens to the concentration profiles in this cases.

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So, let us start with what the concentration profiles work for the case of the fast reaction regime. So, suppose you have a fast reaction regime that is taking place; so again time plotting a as a function of z . So, the fast reaction regime is taking place at fairly large value of root M . You will have a concentration profile like this. And if the concentration if M is far less than q , this would be the concentration profile of b , this would be 1. Now, the moment this condition is no longer valid, that is, as the reaction becomes even faster, let us take another color as this becomes even faster, then a profile starts to develop for b .

So, this is where we are considering the second order case. The concentration of b is no longer uniform up to the gas liquid interface; there is a certain dip in the concentration of b . So, if you look at the profile I have drawn it, such that the concentration gradient goes to 0 at the gas liquid interface and that is the condition that we have. So, that is this condition here that makes me draw a profile of that sheet right.

So, proceeding further, we can imagine that as the concentration profiles become steeper and steeper. So, this is 1. So, concentration profile of b starts becoming more and more pronounced. And so you have the situation where, ultimately for a certain value of root M , the concentration profile of b is such that it hits 0 at the gas liquid interface all right. So, now, in this case, you can see that this is the region where reaction can occur and we

call this as the reaction zone. That is, because it is only in this zone that both a and b are present, outside of this zone only b is present a right.

So, now if you go, if you increase the reaction rate even further, what will happen is that, the concentration profile of b which went to 0 flux at the interface, this gradient of 0 value will penetrate into the film. And therefore, you have a situation which will look like this. So, I have exaggerated things little bit, it is not a that the a has certainly suddenly moved deeper into the liquid. In order to a show the conditions, I have drawn an exaggerated profile of concentration of a, just to show that now the reaction zone has moved into the film right.

Now what happens further is that, this profile gets steeper, this profile also gets steeper. Therefore, the reaction zone starts becoming thinner and thinner. So, it was the entire film to start with at beginning of the fast reaction regime. Then it became thinner and thinner, then the concentration of b started developing a profile, then the reaction zones disengages from the gas liquid interface moves into the film, now it starts becoming thinner and thinner. So, a logical end point to this sequence of figures is reached, when the reaction zone which is becoming, which is being pressed from both side, ultimately shrinks to the point.

So, what we are saying now is that, this is the region where B is present and this is the region where A is present. And where A is present, there is no B and where B is present there is no A. So, the reaction zone is now a plane. So, we can call this as the reaction plane. And, because there is no B here and there cannot be any reaction. So, A will diffuse a without coming up with any consumption within the film. And similarly here B will diffuse without any consumption. So, these are linear profiles. So, this is the A region, this is the B region. So, this is kind of situation that we a meet with, as a limiting case to the sequence of events that we have picture in the last few sketches here.


So, this last condition that we have pictured here, is logically to be called as a case of instantaneous reaction. That is, because there is no region within the film where, A and B can simultaneously coexist, where A is present B cannot exist and where B is present A cannot exist. The moment a molecule of a c is A molecule of B, they annihilate each other and the products is formed. So, this is the bases for calling this is as instantaneous reaction. So, let us see how we can analyze the case of the instantaneous reaction.

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INSTANTANEOUS REACTION REGIME

$0 < x < \lambda$: (A) $D_A \frac{d^2 a_A}{dx^2} = 0 \quad C_A = C_A^*$
 $x=0, a=1; x=\lambda, a=0$

$\lambda < x < \delta$: (B) $D_B \frac{d^2 C_B}{dx^2} = 0 \quad C_B = C_{Bb}$
 $x=\lambda, b=0; x=\delta, b=1$

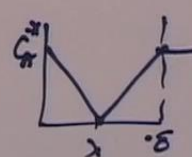


So, in this instantaneous reaction regime; let me give it some nomenclature. So, this point, I will call as x is equal to λ in dimensional distance. So, there is a region 0 less than x less than λ , which contains only A. And here what is happening is the diffusion of A without any reaction. So, this is the governing equation for A in that region. What are the boundary conditions at x equal to 0 , a equal to 1 and at x equal to λ a is 0 .

In the region λ less than x less than δ , we have the diffusion of B. And this is the region that contains only B and no A. So, we have a similar equation, except that, here I must I should have written $d^2 C_A$, because we are writing dimensional variables here and once again this is $d^2 x$ square $d^2 x$ squared equal to 0 and at x equal to λ b is 0 and x equal to δ b is 1 . a is 0 which means that, C_A is C_A^* and here $b=1$ means C_B is C_{Bb} . So, these are the equations. And since both of these have second derivatives equal to 0 , they represent linear profiles of concentration of a with respect to x and concentration of b with respect to x . Now, there this new variable λ here which is unknown and in order to determine that, we examine what is happening at the interface.

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At the position $x = \lambda$

$$\nu N_A = -N_B$$


$$\nu D_A \frac{C_A^*}{\lambda} = +D_B \frac{C_{Bb}}{\delta - \lambda}$$

$$\frac{\delta}{\lambda} = 1 + \frac{D_B C_{Bb}}{\nu D_A C_A^*} = \underline{1 + q}$$

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At the position at the interface between A region and the B region, which is the position x is equal to λ , we should have the flux of A in the in this direction multiplied by the stoichiometric coefficient equal the flux of B in the opposite direction. In other words, A is entering from the left to the right and B is entering from the right to the left and therefore, they are of opposite signs. And the stoichiometric of the reaction, since this is a steady state system, the position of x equal to λ will be constant in time.

Therefore, the rate at which A is being supplied is exactly the rate that is required to consume all of B that is being supplied. So, the ratio of the supply rate of A to the supply rate of B will be in the ratio of the stoichiometric coefficients. So, that is how, that is the basis for writing this equation. And we can write this quite simply by noting that N_A is nothing but $-D_A \frac{dC_A}{dx}$ and this is C_A^* divided by λ , because if you recall the picture, this is δ and this is λ and we have a straight line here and a straight line there.

So, the slope of this straight line is nothing but $C_A^* - 0$ divided by $\lambda - 0$ equal to C_A^* / λ . And the slope of the other straight line is $C_{Bb} - C_A^*$ divided by $\delta - \lambda$. So, this becomes $(C_{Bb} - C_A^*) / (\delta - \lambda)$ when we take out the negative sign there. So, this gives a value for δ / λ which is $D_B C_{Bb} / \nu D_A C_A^*$ or this is $1 + q$ our relative abundance factor that we introduced earlier on in our consideration of effect of reaction on mass transfer.

So, now, let us consider the question of what is the enhancement what is the enhancement?

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Enhancement

$$\frac{N_A|_{rxn}}{N_A|_{No\ rxn}} = \frac{D_A C_A^* / \lambda}{D_A C_A^* / \delta}$$

$$= \frac{\delta}{\lambda} = 1 + q$$

$E_{\infty} = 1 + q$

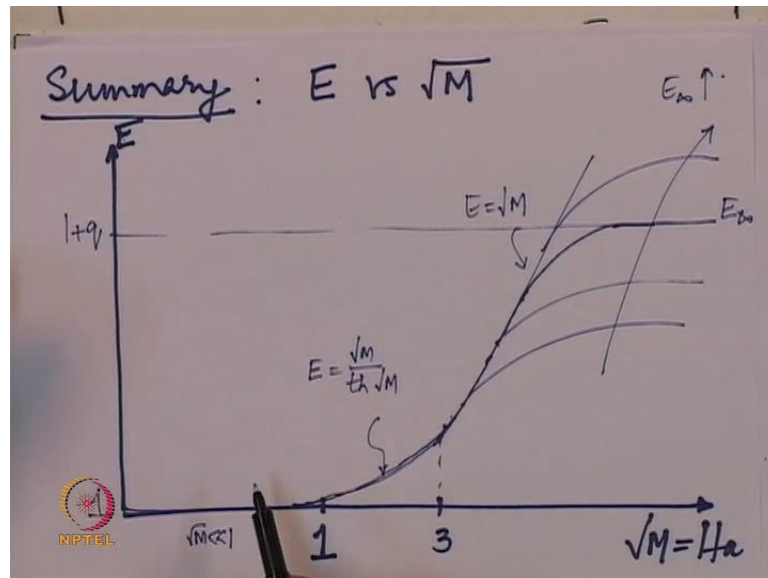
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max value
for a given
System

Enhancement is nothing but the mass transfer rate with reaction divided by mass transfer rate without reaction. With reaction it is $D A C A^*$ divided by λ . Without reaction it is $D A C A^*$ divided by δ . And therefore, this nothing but δ by λ or we have e equal to $1 + q$ because δ by λ was shown as $1 + q$ in the previous slide.

So, this therefore, shows that, the enhancement factor in the case of instantaneous reaction is completely determine this value of relative abundance factor. And for a system, for which the concentration of B is fixed, the concentration of A is fixed. This therefore, represents the maximum enhancement that can occur and therefore, we put a subscript E_{∞} here and this is the enhancement in the case of instantaneous reaction or the maximum value or a given system. Given system in the sense of for system for which the value C_B and fixed value of C_A^* is fixed. So, that completes our discussion of regimes, because for a given system, we have now hit the ceiling on how far we can go in terms of enhancing the mass transfer rate.

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So, now, let us take a look at what we have done. So, far we will summarize in terms of the effect of chemical reaction on mass transfer. And we will do this summary by sketching a plot of E versus square root of M or the effect of Hatta number on the enhancement factor. So, we can make plot like this. On this side, we have enhancement factor, on the this behave the Hatta number also called as root M . We will mark out regions of root M equal to 1 root M equal to 3.

So, we have seen that before for root end values less than 1, we have slow reaction regime. And the enhancement factor is really 1, because you keep saying the physical mass transfer rate. Around 1 the plot starts to lift also this is enhancement factor of equal to 1, around 1 it starts lift of and an about 3; so the equation that governs this part of the curve is $E = \frac{\sqrt{M}}{\tan h \sqrt{M}}$. So, this is our transition regime. Beyond 3, we have this asymptote which keeps on going like that. So, this is your fast reaction asymptote $E = 1 + q$.

Now depending on the system, somewhere here is a value $1 + q$ and that is equal to your E infinity. So, as you keep on increasing root M , the system proceeds along this curve here and at some point it wears away and then goes here. And here of course, it is independent of root M , because instantaneous reaction the rate is so large that we cannot measure it in theory right.

So, depending on your various values of for various systems these asymptotes will occur at various points and therefore, this is the direction and which E infinity will increase. As you increase the value of E infinity, the maximum value of enhancement factor that you can get increases. So, we will stop at that point. We will talk a little bit more about the slow reaction regime, in order to fill out some detail on this plot, when we come back. And then, we will take it further to investigate; what the surface renewal theories have to say about the same regimes that we have considered within the frame work of the film theory.