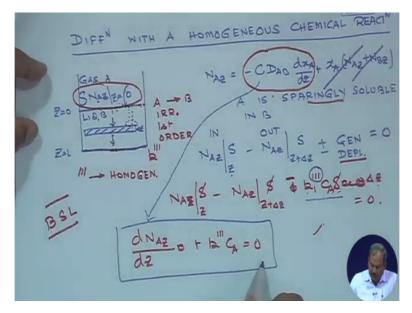
Transport Phenomena. Professor Sunando dasgupta. Department of Chemical Engineering. Indian Institute of Technology, Kharagpur. Lecture-45. Mass transfer (Continued).

We were discussing about diffusion, probably with convection in a system in which there is a homogeneous chemical reaction taking place. So the problem which we have attempted in the last class is about a gas which gets dissolved in a liquid and then it starts its decision towards the other end of it. So it could be a solid container in which a liquid B is kept and A gets slowly dissolved at the top and A molecules as it starts moving towards the bottom of the container, it reacts with B, therefore destroying A in the process and we wanted to find out what is the distribution of concentration of A in the solution, in the solution of B which is kept.

So we wanted to know what is the concentration distribution of A in the liquid. And of course the maximum concentration would be at the top where A gets dissolved and as we move progressively downwards, the concentration of A will slowly get will slowly get diminished. So since it is a homogeneous reaction, the term would appear in the governing equation itself as a source or sink term. So if we if we take a slab of the liquid and the amount of A in moles or mass, let us say in moles, amount of moles of A coming in at the at the top of the slab and the amount of A that goes out, so in - out and since it is a reaction in which A gets consumed, so - of, - of the depletion should be equal to 0 at steady-state.

So in - out + or - generation or depletion would be equal to 0. And we assumed the order of the reaction, so the amount of A that comes in, the one that goes out, the amount of A that comes in was NA which is a molar flux multiplied by S, where S is the cross-sectional area of the assumed shell. So this is what we have done in that class.

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So the amount of A which comes in which is N AZ which is evaluated at some location Z times S where S is the cross-sectional area - the flux evaluated at the other end of the assumed slab multiplied by the same cross-sectional area + or - generation or depletion and the depletion term was simply K1, note the triple prime which denotes that it is a reaction which is homogeneous in nature. So K1 triple prime represents a homogeneous reaction and since it is first-order it is going to be K1 triple Prime CA times S where S is the cross-sectional area and delta Z where the thickness of the assumed shell is delta Z.

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$$\begin{aligned} \begin{bmatrix} -D_{AB} \frac{d^{2}C_{A}}{dz^{2}} + b^{|||}C_{A} = 0, \\ \hline dz^{2} = 0, \\ \hline dz$$

So dividing both sides by delta Z, we got this as the differential equation, governing equation. And after putting in the expression of N AZ, using Fick's law and assuming that it is a onedimensional diffusion only case, where A diffuses in the Z direction, so this was the form of the equation and the 2 boundary conditions that we have used were at Z equal to 0, that means that the liquid air interface, the concentration of A is maintained at CA 0, where CA0 is the, could be the interface solubility, the solubility of A in the liquid. And at the other end what we have done is that at Z equal is L, that means at the other end of this system, since this layer is impervious to the A molecules, so the flux of A at that point would be equal to 0 and therefore dCA dZ would be 0.

So it acts like an adiabatic wall in the case of heat transfer. So the concentration this tradition was obtained in cos hyperbolic form where the constant BA is nothing but this. And the average concentration is obtained by averaging over the entire length of the liquid pool, so between 0 to L and dividing it, divided by, dividing it by L, so this when plugged in here would result in the average concentration of A inside the liquid pool of B, where this B 1 is simply a constant.

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What we are going to do in this class is we are going to look at what would be the form of the, what would be the governing equation and the relevant boundary conditions if we have disillusioned with a heterogeneous reaction. So we can either have a slow reaction have a fast connection. So 1st initially what we are going to do, we are going to do with a fast heterogeneous reaction, therefore this will be our problem 1 and the slow heterogeneous direction would be our problem 2.

So the 1st thing is what we are going to do, we have a very fast reaction in which the product, the moment it reaches the heterogeneous surface, heterogenous reaction and heterogeneous, perfect example of heterogenous reaction is a catalyst, catalytic reaction, where you have catalyst particles present in it, so a species will travel through the film, the thin film which surrounds, thin film of of the of a gas which surrounds this catalyst pellet, reaches the surface and immediately upon reaching the surface the reaction, the instantaneous reaction takes place and whole of A gets consumed, gets converted to some products.

But as it diffuses through the film, through the thin film, nothing happens to A. So it is a diffusion only that is taking place in the thin film without it is getting converted to any product. The conversion comes only at specific location in the system, that means the catalyst pellet. Since there is no distributed generation or distributed d depletion of A as it travels through this thin-film, the reaction term will not does not appear in the governing equation. The governing equation will be considering only a diffusion, it is a diffusion only case when we have a thin-film.

The surface reaction will come as a boundary condition while solving the governing, while solving the governing equation. So we will see that and the example that we are going to do as that of a catalytic reactor. We all know that catalytic reactors are added to cause, in order to convert the toxic gases, like say, so the gases and to convert them from the lower oxides to higher oxides of carbon, nitrogen and so on.

So carbon monoxide coming in to this catalytic reactor, so this is a catalytic reactor, example could be in a car where we have a gas A which comes in and there are catalyst particles distributed everywhere where A gets converted to let say A2 and then what you are going to get out of this is gases A and A2. So the reaction that takes place as 2 molecules of A will react on the catalyst surface to produce one molecule of A2. So this is the reacted, this is the product. Now these catalytic particles at times fundamentally it is easier to handle if you assume that the catalyst surface looks something like this. So this is the catalyst surface on which the reaction takes place, so this is the catalytic surface which is surrounded by a thin stagnant film.

So this is at Z equals delta and this is at Z equals 0. So what you have here is then A molecules are moving over this stagnant film that surrounds the catalyst surface, so A starts refusing in this direction, the reaction from A to A2 takes place on the surface and A2 starts diffusing back towards the bulk stream of the gas mixture which is going. So here you have A + A2. So this is the, this is the edge of a hypothetical gas film which exists around each particle or in other words the conceptual modelling tells us that each particle is surrounded by a stagnant gas film through which A diffuses to reach the catalyst surface, it gets converted into the product A2 and then A2 starts moving back, its journey back towards the bulk flow where both A and A2 gets carried away towards the exit of the catalyst reactor.

So this is a simplified modelling of the catalytic reactor that is taking place, that we are attempting here and we are trying to find out what would be the concentration profile of the reactant A in the stagnant gas film. And once we have the concentration profile then we would be able to convert that, we would be able to deduce from that what is the conversion rate of A to A2 and that would help us in designing such a catalytic reactor. So that is the practical example use of such a modelling exercise and we would like to do that over here.

So we also know that for each molecule for one mole of A, so one mole of A2, 2 moles of A moves in the + Z direction. So for one mole of A2 moving in the - Z direction, we have 2 moles of A which is moving in the + Z direction. So 2 moles of A coming and getting over

here to form A2, so 2 moles of A has to move in the + Z direction for one mole of A2 to move in the - Z direction. And at steady-state the rate at which A comes in, so 2 moles of A comes in and the rate at which A2 moves out must be equal.

So in other words what we can say is N A2 Z, that is the molar flux of A2 in the Z direction must be equal to - half of the molar flux of A in the Z direction. So this is the direct result of this stoichiometry of the reaction in which 2 moles of A reacts to form one mole A2. So therefore in flux term with the introduction of appropriate sign I can write that N A2Z is equal to - half of N AZ. And starting with the formula that NA is equal to - C DAA2, this is the diffusion coefficient of A in A2 times dXA dZ + XA times N AZ + N A2Z. So this is the Fick's law and here we know what is the relation between N AZ and N A2Z from here.

So substituting the expression of N A2Z from this to over here, what we can get is N AZ equals - C, the diffusion coefficient of A in A2 by 1 - half of XA multiplied by dXA dZ. So this is now the correct form of the flux of A in the Z direction. And the stoichiometry of the reaction gives me the relation between NA and N A2, so this is my flux reaction. As before I can think of a thin shell over here and NA is coming at N AZ at Z and the one that goes out would be N AZ evaluated at Z + delta Z. Since no reaction is taking place in here, the conversion, the equation would be simply in - out at steady-state would be equal to 0.

So what I would get out of this is N AZ multiplied by the cross-sectional area of this assumed slice evaluated at Z - N AZ at this point evaluated at Z + delta Z times S is going to be equal to 0. So in - out is equal to 0 since no reaction is taking place in here. Reaction is only taking place on the catalyst. So you can divide both sides by delta Z and the governing equation out of this would simply be, will simply be equal to d dZ of N AZ is equal to 0.

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So this is the governing equation for the modelling exercise which we were doing. And when you plug-in the expression for N AZ it would simply be, when we plug in this expression for N AZ into this, what we would get is that a d dX of 1 by 1 - half of XA times dXA dZ will be equal to 0. Had this been a case of diffusion only situation, that is, A is moving towards the Z, towards the catalyst surface by diffusion, only by diffusion, in that case the 2nd terms, that means this term on the right-hand side, this term on the right-hand side of the, of the species balance equation, this entire term would be 0 and NA would be equal to the diffusive flux.

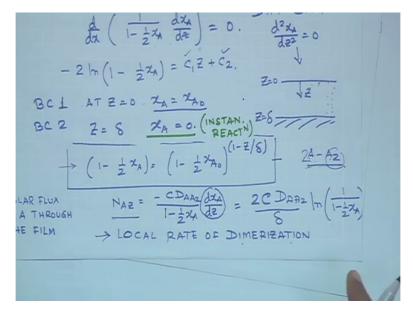
So if NA is reaching the catalyst surface by diffusion only process, then your governing equation, this entire term 1 by 1 - half XA would not be present. So you would simply get d2 XA by dZ square equal to 0 and you would get a linear profile, linear profile of A in such a system. So for a diffusion only case, this equation would get transformed to d2 XA by dZ square to be equal to 0 and this can be solved. So once you solve this equation the solution of this equation is going to be one 2 ln 1 - half of XA is equal to C1 Z + C2. And the boundary conditions 1 and boundary conditions 2, the one is going to be at Z equal to 0, that means this is my catalyst surface, this is Z equal to 0 and this is Z equal delta and this direction we have the Z.

So at Z equal to 0, XA, the mole fraction of A is some known value XA to be equal to XA0. So one condition that we have for the film is that the concentration at the outer edge of the film, the bulk flow is known to me. So the concentration at X equal, at Z equal to 0 is some known value XA 0. But it is interesting to see what what would be the boundary condition at the other end, that is on the catalyst surface. As I have mentioned before, on the catalyst surface A instantaneously gets converted to 2 A2. So that means on the catalyst surface, there cannot be any free A present.

Or in other words, the concentration of A on the catalyst surface must be equal to 0, which is true only if the reaction rate is very high or it is, there is an instantaneous reaction. So A immediately gets converted to A2. So for such conditions the concentration of A on the catalyst surface would be equal to 0. And therefore the 2nd boundary condition in this case would be at Z equal to delta XA equal to 0. So this is true, since we have an instantaneous reaction. It is an instantaneous or very fast direction, so XA is going to be equal to 0.

So when you plug these 2 boundary conditions and evaluate C1 and C2, what you get as a final form is 1 - half of XA is equal to 1 - half of XA 0 to the power one - Z by delta. So this is going to be the distribution of mole fraction of A in the thin-film as a function of Z, as a function of the thickness of the film which surrounds its each particle and the concentration of A in the free stream condition.

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This is fine but we are probably more interested to know what is the molar flux, what is the molar flux of A through the film. So the molar flux of A through the film and we understand that N AZ is constant. So this is essentially gives you N AZ is constant, since N AZ is constant, you can evaluate N AZ at Z equal to 0 or Z equals delta it does not matter for any point in between. So your N AZ would be equals, from the previous equation D diffusion coefficient of A in 2, 1 - half of XA from our previous relation times d XA dZ.

And this dXA dZ evaluated from this would simply be equals twice the concentration, the total consecration of both A and A2 present in the film, the diffusion coefficient times delta logarithmic of 1 by 1 - half of XA. So this is the rate at which A is approaching, A is moving towards, in the in this film towards the surface. Now the reaction A giving A2 is simply a dimerisation reaction. 1, 2 moles of A, twice A giving A2, that was the reaction which we have used. So it is essentially 2 molecules of A, 2 moles of A are forming a dimer A2. So since at steady-state whatever be the rate at which the molar flow rate of A coming towards the surface, that gets converted into A2.

So N AZ can also be written as, this is the local rate of dimerisation. So the flow of A, the molar flux of A is essentially the rate at which A is going to form the product which is a dimerisation reaction. So this is going to be the local rate of dimerisation of A into the product. So this is a concrete example of what happens when we have the reaction that is taking place on the catalyst surface, on a heterogeneous reaction. A slight variation to this problem can be given if instead of an incident a reaction, if it is a slow reaction. That is the rate of conversion of A to A2, the rate constant is not infinite, it is finite.

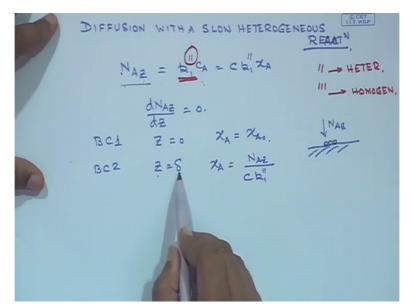
So therefore the rate at which A gets converted to A2, it has a finite, it has a finite rate. So it is dictated by a rate expression by rate constant which is not infinite. So the next step, the next extension of this problem can be if we need to find out what is going to be the profile and what is going to be the rate of dimerisation if instead of a very fast action, we are dealing with a slow reaction, everything else will remain same. Since no reaction is taking place in the bulk, therefore the governing equation will be, will remain unchanged. So therefore d dZ of N AZ will still be 0, that is your governing equation.

The expression for N AZ in terms of Fick's law, that will also remain the same since the stoichiometry is same, so for each 2 moles of A coming towards the catalyst surface, one mole of A2 has to travel in the reverse direction. Okay. So that relation will also remain unchanged. So my governing equation will remain unchanged, the expression by which N AZ can be replaced in the governing equation will also be the same. The only difference that we would see is what is going to be the boundary condition on the catalyst surface. Previously we took the boundary condition of the catalyst surface to be that the concentration of A on the catalyst surface is 0.

No A can exist on the surface. But since it has a finite rate of reaction right now, so we have to take that into account in our description of the 2nd boundary condition of the problem. So

the next problem extension of this problem that we are going to do is what is going to happen if it is a slow reaction.

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So the reaction, the problem that we are going to do is the diffusion with a slow heterogeneous reaction. So let us say that the rate at which A disappears on the surface is given by this rate expression. Remember the note the double prime that I have used for the rate constant. So double Prime is for heterogeneous reactions and as I mentioned before, triple prime for homogeneous reactions. So this is a double prime which is conventionally used for this case. So the governing equation will remain the same as I have said before, d dZ of N AZ to be equal to 0.

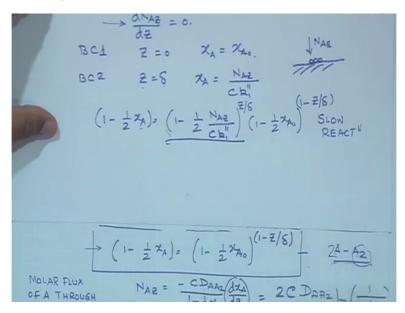
And the boundary condition 1 will remain unchanged, that is at Z equal to 0, XA is equal to some known consecration, some known mole fraction XA0. The boundary condition able to which is that Z equals delta, previously the boundary condition that we have used is XA to be equal to 0, then what I am going to use here is XA is N AZ divided by C K1 double prime. At steady-state the flux of A coming towards the catalyst surface, this is the catalyst surface, the A which is coming, the N AZ, the flux of A which is coming towards the catalyst surface and it is getting consumed on the catalyst surface.

So the rate at which A comes in towards the catalyst surface must be equal to the rate at which it gets converted into products. So if this does not happen, so the amount of A that comes in from the bulk towards the catalyst surface and the rate at which it gets converted to products, if these 2 rates are not equal, then what is going to happen is that the concentration

of A on the catalyst surface will keep on changing with time. So if we have more of A coming towards the surface than getting converted to A2, then with time the concentration of A on the catalyst surface will increase.

And if less of A is coming, then the rate at which it gets converted, then the amount of A, concentration of A molecules of the cattle surface will decrease with time. Both of them violate our steady-state assumption. That is the concentration of A or A2 is a function only of Z but it is not a function of time. So a steady-state can be attained only when the flow, the molar flow of A towards that catalyst surface is equal to the rate at which it gets converted into the products. So therefore using equating the flux to the reaction rate, the flux of A in the Z direction to the reaction rate, I can, we can write the condition at Z equals delta, the equality of the rate of movement of A to that of the reaction rate, this is the condition that one can write.

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And when you solve this and the boundary, the governing equation will remain the same, so when you plug that, plug the expression of N AZ exactly like the previous one into this and integrate and use the conditions, boundary conditions, the final form that you are going to get is, so this is going to be the expression, this is going to be the expression for expression for the concentration distribution of A in the Z direction. Just compare this with the expression which we have obtained when it was an instantaneous reaction. So this is for a slow reaction and this is for an instantaneous reaction.

So compare these to and you would see that this one, these terms appears additionally, this additional term appears in the expression of concentration distribution of the mole fraction, concentration distribution or the variation of mole fraction as a function of Z. So comparing these 2 you would see that this is the additional term that comes because of the nature of the reaction being slow as opposed to instantaneous as in the previous case. So you can evaluate N AZ as we have done before and this N AZ, the expression for N AZ would simply be equal to twice C, the diffusion coefficient of A A2 divided by delta ln of 1 - half N AZ by C K1 double Prime divided by 1 - half XA 0.

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RATE OF DIMERIZATION 2C DAA2 8

So here you can again see the difference between these 2. So this term remains the same, this term remains the same but this one, this one over here, this one over here, the derivatives are same but the numerator is different. So this is the, this is the rate of conversion of A, rate of conversion of A in terms of the other parameters. Since this is logarithmic, if this term is small, the logarithmic, logarithm of the numerator can be expressed in the Taylor series and considering only the 1st term, slight simplification of this equation can be maintained, can be obtained which would give you N AZ to be equals twice C D A A2 diffusion coefficient by delta 1 + diffusion coefficient divided by K1 double Prime delta ln 1 by 1 - half XA 0.

This is the form which you would obtain when you take it Taylor series expansion of this. Okay. So again compare the results which we have opted with the result that we we opted before, that is the local rate of dimerisation for a fast reaction is simply twice C D A A2 by delta. So we have this over here but this is the additional term that we are getting since our reaction rate is finite. Had this been an infinite reaction rate, signifying that it is an instantaneous reaction, then this whole term would be 0 and this expression would revert to whatever expression we have obtained for the case of very fast reaction.

So it is always better to see that in the limiting case where the value of K1 is very large whether or not this expression becomes the same identical with the expression which we have derived based on an infinite are very large reaction rate, instantaneous reaction. So this is, this is consistent with our understanding. And the dimensionless group, dimensionless group D A A2 by K1 double Prime delta which is this, this has to be dimensionless and this dimensionless describes the effect of surface reaction rate on the overall diffusion reaction process.

The previous result which we have obtained for the case of 1st reaction was a d diffusion which is taking place. But here the process is governed not only by diffusion, also by the reaction, the rate of reaction which is taking place on the catalyst surface. And the term, the group, the dimensionless group which is responsible which is an indicator of the effect of reaction in this diffusion process is essentially what we have in the denominator, the diffusion coefficient of A in A2 divided by K1 double Prime delta.

Because if we did not have this, if this is equated to 0 then you the expression becomes identical to this one, this expression becomes, sorry this expression becomes identical to this one. So therefore the dimensionless form D A A2 by K1 double Prime delta, it denotes the effect of surface reaction on the overall diffusion reaction process. So what we have done here is and whatever I have taught in this class, it is also available in Bird, Stuart and Lightfoot. As I told you before in this part of the mass transfer, treatment of mass transfer I am following the textbook Bird, Stuart and Lightfoot.

Whenever I am going to do something different from another book, I will let you know. But all the examples of mass transfer that we have analysed so far are given in your textbook transport phenomena by Bird, Stuart and Lightfoot. So what we saw is that using a shell mass balance and with the appropriate boundary conditions, incorporation of reaction rates as a source come in the governing equation for a homogeneous reaction or as a boundary condition in heterogeneous reaction we could solve, we could obtain the profile, the concentration profile or the mole fraction profile of any component in as a function of position. And the heterogeneous reaction that we have analysed, we took 2 extreme cases, 1 when the reaction is instantaneous and 2^{nd} when the reaction has a finite rate, that means it is a slow reaction.

So this probably has given us enough information for us to have a too have a tutorial in the next class in which we will solve some of the problems of mass transfer of similar nature but with slightly more complexity.