**Heat and Mass Transfer**
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Lecture No. 34
Introduction to Mass Transfer - 2

Welcome back to the second lecture on mass transfer. In the previous lecture, after a brief introduction we studied the Fick's law of mass diffusion its various forms. We also noted its similarity with the Fourier's law of heat conduction. Then we looked at some tabulated values of the diffusion coefficient D, then we studied mass diffusion in a stationary medium, steady state one dimensional cases and near the end of the lecture we solved a problem of hydrogen migration through a steel plate. Now let us move on to the study of diffusion in a moving medium.

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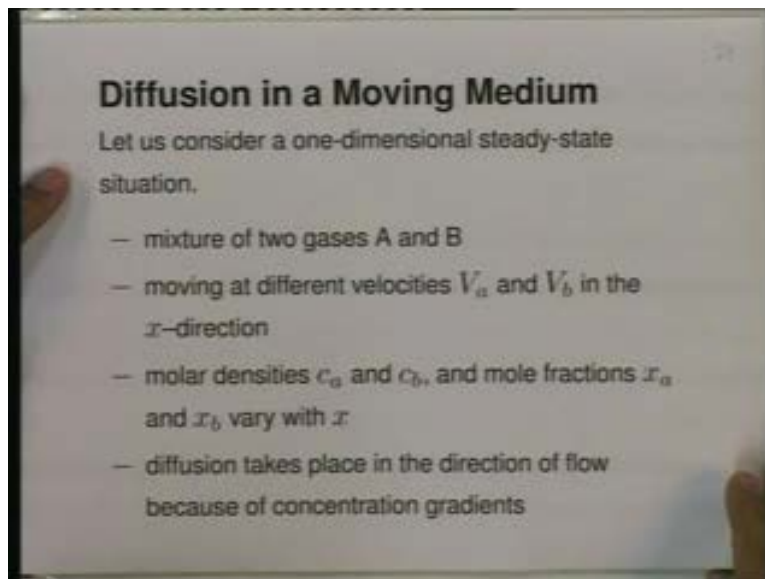
Again, for simplicity, for the study of diffusion in a moving medium, we will consider one dimensional and steady state situations; this will keep the analyses simple and straightforward. Again, for simplicity we will consider a mixture of 2 gases say A and B. We will assume that the thing is not stationery, the gases are moving at different velocities in the x direction; let V_a with the velocity of component A and V_b be the

velocity of component B. Let the molar densities at a particular location of the gases be c_a and c_b kg mole of a per meter cube kg, mole of b per meter cube and the corresponding mole fractions be x_a and x_b and it is possible that V_a, V_b, c_a, c_b, x_a, x_b vary with x because it is one dimensional situation.

Now, there is direction of flow but over the direction of flow, over the bulk movement, there is a diffusion taking place because of the concentration gradients. We are assuming that c_a c_b, x_a, x_b are varying with x. We begin by defining an average velocity; let us define the molar average velocity.

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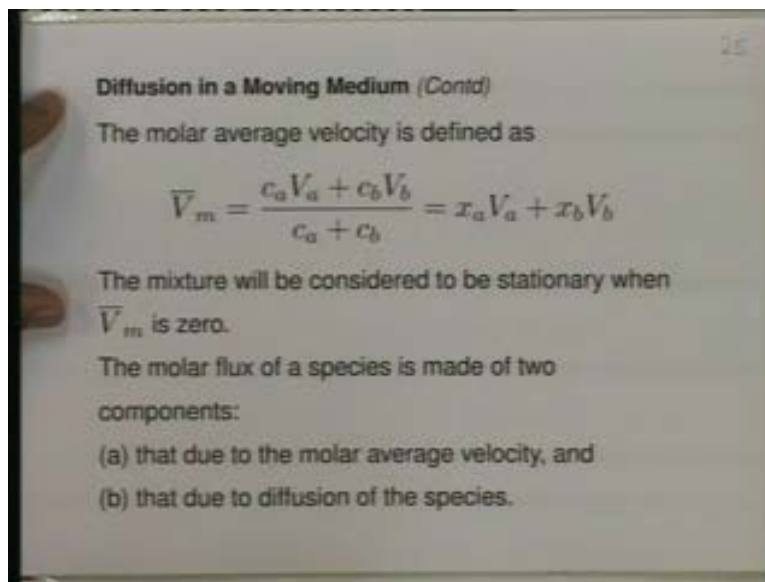
The molar average velocity V bar m - this is defined as c_a into V_a plus c_b into V_b divided by c_a plus c_b - if some slot of weighted average, the weights are the molar densities of a and b. In terms of mass fraction this can be written down as x_a V_a plus x_b V_b and we will consider the mixture to be stationery when the molar average velocity, it is 0. Notice that the molar average velocity may be 0 when V_a and V_b are non-zero but have different signs. So, if the bulk movement of a is say from the left to right, bulk movement of b is from right to left, it is possible that the magnitudes V_a and V_b are such that they cancel out with averaging and V_m m bar could be 0.

Now we should remember that the molar flux of any species will be made up of 2 components. Because of the molar average velocity, the whole mixture - whole system - is drifting either to what is the right or to the left and hence the molar flux of any species will be given to the molar average velocity in part but there will also be component due to diffusion of the species. So these 2 will get super imposed over each other and we will have a total molar heat, molar flux with this super-imposition; it is now possible to write down the molar flux of species A.

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Diffusion in a Moving Medium *(Contd)*

Since

$$\left(\frac{\dot{N}}{A}\right) = \left(\frac{\dot{N}_a}{A}\right) + \left(\frac{\dot{N}_b}{A}\right)$$

hence

$$-cD_{ab}\frac{dx_a}{dx} = cD_{ba}\frac{dx_b}{dx}$$

But since $x_a + x_b = 1, -(dx_a/dx) = (dx_b/dx)$.

Hence

$$\boxed{D_{ab} = D_{ba}}$$

That would be N dot A per unit area; the units here will be kilo mole of A per second per meter square. So, kg mole a per meter square second - that will be the molar density of A multiplied by the mean molar velocity. This is due to the bulk motion and this is modelled by Fick's law - the diffusion in the x direction of species a. So, the bulk movement component and the diffusive component, you can also say convective component and diffusive component. In a similar fashion, for species B we can write molar flux of species B kg mole of b per meter square per second will be in part due to the bulk movement of species B because of the molar average velocity V bar m that would be c_b V bar m. Add to that minus c D_{ba} dx_b by dx which is the diffusive component; the second term here as well as second term here is represented using the

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Fick's law of diffusion and notice that in this equation it is D_{ab}. The diffusion coefficient of a diffusing through band, this is D_{ba} - diffusion coefficient of b diffusing through a. We will soon come across a very useful relationship between D_{ab} and D_{ba}.

In these expressions, it is not necessary that the molar density of the mixture c be uniform but if it is uniform or constant, then the expressions which we just saw can be replaced by slightly simpler forms not in terms of mass fractions as in this case - x_a and x_b - but in terms of mole molar densities c_a and c_b; these are the expressions except that c being a constant, we can move it inside the derivative sign. So, we have the right hand side for the first equation in terms of c_a, the right hand side in the second equation in terms of c_b. We now write an expression for the total molar flux combining species a and b together; we should remember that the total molar flux is made up of the molar flux for component a plus the molar the molar flux for component b. If we add the 2 expressions, one for molar flux of a and another for molar of b and use the definition of the molar mean velocity, we will get this expression which represents a relation between the gradient of x_a, the gradient of x_b and D_{ab} and D_{ba}.

Now, we should notice that x_a and x_b are mole fractions in a two-component mixture. So their sum is 1 and hence the derivative of 1 will be equal to negative of the derivative of the other and because of this, this expression simplifies to an important expression - D_{ab} is D_{ba}. This is an important relation which indicates that the diffusion coefficient for species a through b equals the diffusion coefficient of species b through a. Now at this stage we should remember that we have defined a molar average velocity. It is possible for us to define a mass average velocity so instead of V bar m we may define a V bar the mass average velocity which will be the mass density of a into V_a plus the mass density of b into V_b divided by the sum of the mass densities which is the total density.

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$$\overline{V} = \frac{\rho_a V_a + \rho_b V_b}{\rho_a + \rho_b} = w_a V_a + w_b V_b$$

$$\overline{V}_m = \qquad\qquad x_a V_a + x_b V_b$$

In general

$$\overline{V}_m = 0 \quad \text{does not mean} \quad \overline{V} = 0.$$

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If the mass fraction is represented by our symbol w, then this is $w_a V_a$ plus wb V_b. Now, notice that this is the mass fraction average velocity whereas we had V bar molar equal to $x_a V_a$ plus $x_b V_b$; in general, mass fractions are not equal to mole fractions and hence there is no reason why in a general case the average velocity should equal the molar average velocity. So, in general these 2 average velocities will be different and that also means that in general the case of V_m equal to 0 does not mean V bar equal to 0. So if the molar average velocity is 0 and the mixture is stationary in that it does mean that the mass average velocity is 0 and also if the mass average velocity it is 0, it does not mean that the mole average velocity is.

So, whenever we do our mass transfer analysis, it will be important to note which average velocity we are talking about because they are different and should be treated in a different way. Now, we move on to the next case which is again a one dimensional steady state situation and which is known as equimolar counter diffusion. In equimolar counter diffusion, we look at a situation which is like this.

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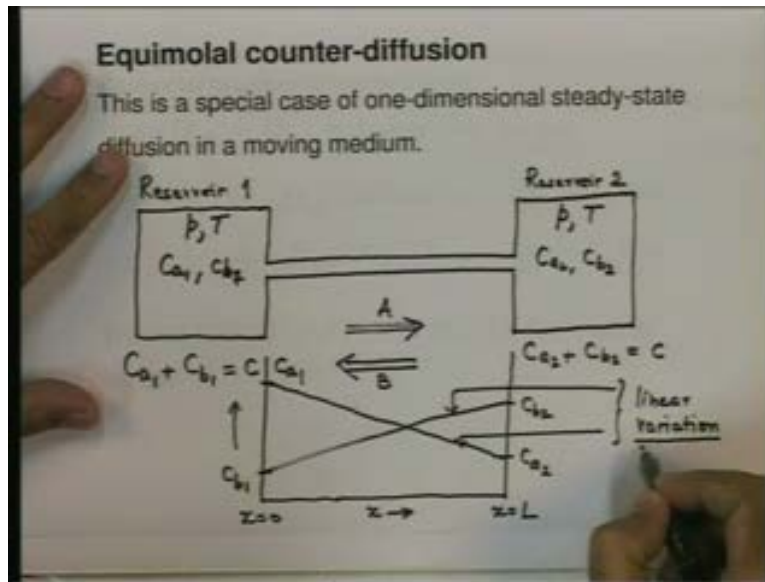
Let me sketch it. We consider 2 large tanks or reservoirs, let us say this is reservoir a and we have here another large reservoir b and let us connect the 2 reservoirs by thin long duct. This is reservoir 1 and we assume that the 2 reservoirs are large enough so that a small amount of mass moving out of reservoir 1 into reservoir 2 and vice versa does not really change the state and the concentration in reservoir 1 nor does it change the state or the concentration in reservoir 2.

In the case of equimolar counter diffusion, we assume that both the reservoirs are at the same pressure p and also at the same temperature t. They contain a mixture of 2 gases - assume ideal gases - the concentration is different in reservoir 1 and in reservoir 2. Let us say the 2 component a and b, then the molar densities in the reservoir 1 are c_{a1} and c_{a2} and c_{a1} and c_{b1} and the molar densities in the reservoir 2 are c_{a2} and c_{b2}. Since the pressure and temperature are the same in both the reservoirs and if we assume them to be ideal gases - the components - we can show that c_{a1} plus c_{b1} it is c. And c_{a2} plus c_{b2}, the total molar density in the second reservoir will also be C because each component is assume to be an ideal gas and the pressure and temperature in each of the reservoir is the same.

Let us plot against the distance x, let us say this is x equal to 0 and this is x equal L - the length of the thin passage between the 2 reservoirs - and let us plot concentration on this axis and let us say that the concentration of a c_{a1} in the reservoir 1 is higher than concentration c_{a2} in the reservoir 2. Let us also assume that concentration of c_{b2} in reservoir 2 is higher than the concentration c_{b1} in reservoir 1. Our aim is to determine the variation of concentration for a and b between reservoirs 1 and reservoirs 2 along the connecting passage. The way we have assumed things, c_{a1} is higher than c_{a2}, so there will be a diffusion of component a from reservoir 1 to reservoir 2 and there will be a diffusion of component b from reservoir 2 to reservoir 1. Our aim is to obtain relations for these rates of diffusion and also obtain relations for the concentration profiles in the duct connecting reservoir 1 to reservoir 2. We proceed as follows. We have already assumed that the 2 components are ideal gases or obey the perfect gas law.

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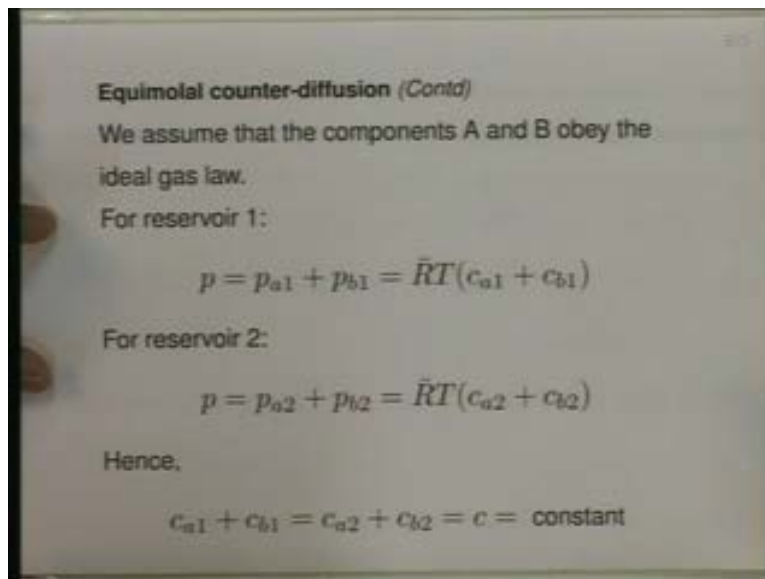
Because of this we can write the molar concentrations directly in terms of partial pressure.

Let us look at reservoir 1 - the total pressure of reservoir 1 is made up partial pressure of component a, partial pressure of component b. And in terms of the universal gas constant

R bar we get the left hand side equal to R bar T into c_{a1} plus c_{b1} R bar T into c_{a1} is Pa_1 R bar T into c_{b1} is P_{b1} - that is the ideal gas law. A similar expression for reservoir 2 gives p. We have assumed the same pressure for reservoir 1 and reservoir 2 so p will also equal p_{a2} plus p_{b2} which is R bar T into c_{a2} plus c_{b2} because we have assumed the same pressures in either reservoir. From this, it turns out that c_{a1} plus c_{b1}, that is the total molar density in reservoir 1 should equal c_{a2} plus c_{b2} which is the total molar density in reservoir 2 which is c; which should be a constant because the number of moles and molar density in reservoir 1 must equal that in reservoir 2 at any time during the process because the pressure remains constant.

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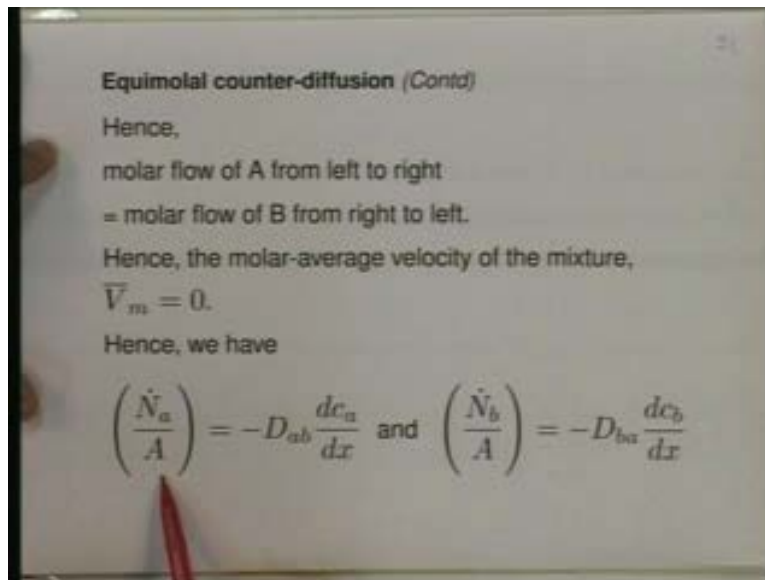
We have assumed the reservoirs to be large enough; this implies that the molar flow rate from left to right must equal the molar flow rate of B from right to left. That means if 1 mole of A diffuses say in10minutes from reservoir a to reservoir b in the same10minutes 1 mole of b will have to diffuse or will have diffuse from reservoir b to reservoir a. This characteristic gives this process the name equimolar counter diffusion and because the number of moles moving from left to right and number of moles moving from right to left are the same, the molar average velocity of the mixture will be 0 because number of moles moving from left to right and number of moles moving from right to left are the

same. Hence, in our expressions for the molar flux of a and molar flux of b, we will not have the term containing V_m bar because V_m is 0.

So, we have the molar flux of a provided by the Fick's law minus D_{ab} D_{ca} by dx and molar flux of b is also minus D_{ba} D_{cb} by dx. We use this expression because we have already demonstrated that the total molar density c is a constant; so, we can write this in terms of D_{ca} by dx and D_{cb} by dx. Again, we will make use of the fact that D_{ab} equals D_{ba}. We integrate these 2 equations which we saw just now - one for D_{ca} by dx and one for D_{cb} by dx. Since everything is isothermal and at constant pressure, it makes sense to know that D_{ab} is a constant, D_{ba} is also a constant. So, the integration is straightforward and if we integrated from x equal to 0 which is the connection of the duct to tank or reservoir a to x equal to L which is the connection of the duct to reservoir b we will get expression - the molar flux of a in terms of the molar density of a in the 2 reservoirs and using the ideal gas law in terms of the partial pressures of a in the 2 reservoirs.

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And a similar expression for the molar flux of b but we also have the molar flux of a equal in magnitude but opposite in direction to the molar flux of b. So this is the negative of this from which it make sense to relate c_{a2} minus c_{a1} to c_{b2} minus c_{b1} and p_{a2} minus

p_{a1} to p_b to minus p_{b1}. Again integrating it not from x equal to 0 to x equal to L but from x equal to 0 to some intermediate value of x, we get profiles for the variation of molar density of a and the variation of molar density of b in terms x and L. And this expression indicates that what we sketched here the variation of molar density from x equal to 0 to x equal to L; these relations or these variations are linear. So this leads to simple expressions; knowing the molar concentrations of a and b, we can determine the molar density profile but more importantly we can determine the molar flux of a and the molar flux of b.

Let us solve a problem so that our ideas are clear. Although our derivation is for large tanks, it is equally applicable to a tank which is exposed to the ambient to the atmosphere through a passage - thin long duct. So here, I will read out the problem.

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Problem

A large tank contains ammonia gas at 1 atm pressure and 25°C. A long open tube, 1 m long and 5 mm in diameter, connects the tank to the air outside, which is at the same pressure and temperature. Make any reasonable assumptions and calculate (a) the rate at which ammonia is lost through the tube, and (b) the rate at which air enters the tube.
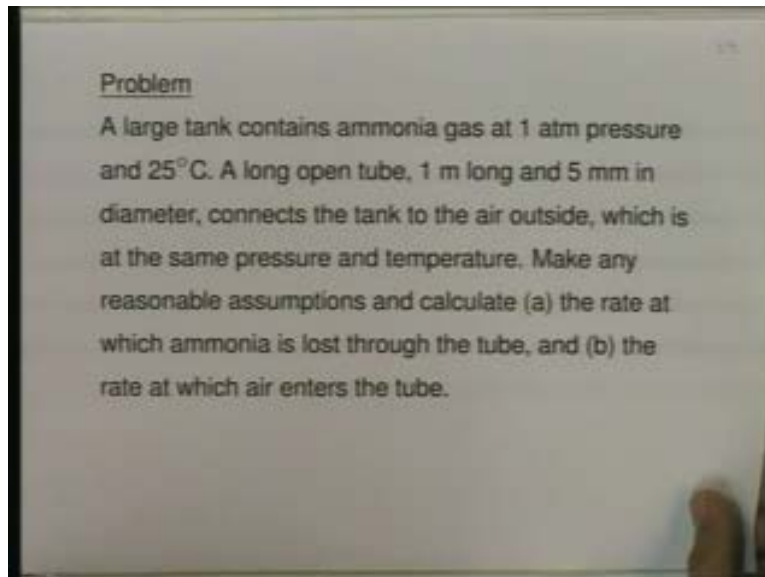
We have a large tank which contains ammonia gas at 1 atmosphere pressure and 25 degree C. A long open tube, 1 meter long and 5 millimeter in diameter, connects the tank to the air outside and the ambient air is also assumed to be at the pressure of 1 atmosphere and temperature of 25degree C. We will make some reasonable assumptions and then we are required to calculate the rate at which ammonia is lost through the tube

because the tube is exposed to the atmosphere. And b - the rate at which air enters the tube. Let us sketch the situation.

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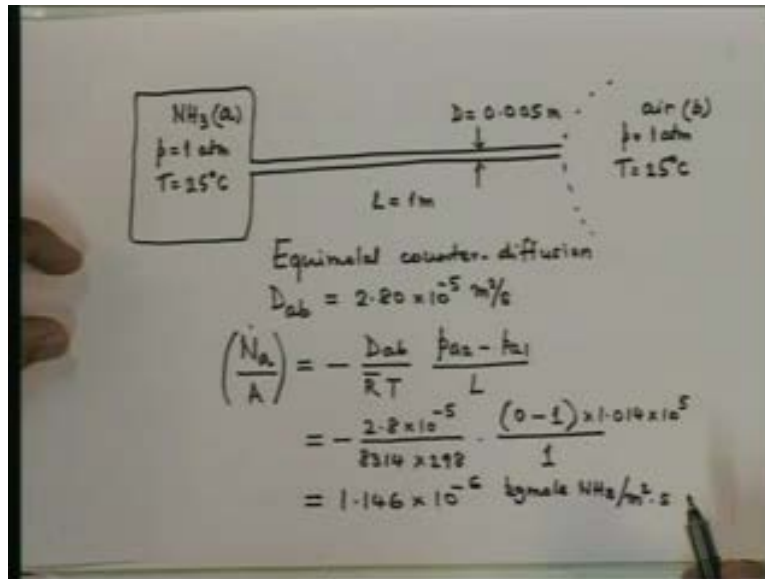
We have a large ammonia tank and it is connected to the atmosphere through a 1 meter long tube so L equals 1 meter. So that tank here is actually open to atmosphere; this contains ammonia, the pressure is 1 atmosphere, temperature is 25 degree C. Air in the surrounding atmosphere to which the duct is exposed here to the pressure is 1 atmosphere and temperature is 25 degree C.

The connecting duct has, small diameter D is 5 millimeters, .005 meters. We have to determine the rate at which ammonia diffuses through the duct. And air leaks into the tank because the pressures are the same, the temperatures are the same if we assume air as well as the ammonia vapor to behave like ideal gases. This is case of equimolar counter diffusion; the duct is narrow and long so we will assume a one dimensional situation and we will also assume that a steady state exists. So when the ammonia is open to atmosphere there may be a sudden rush of ammonia, that initial part we are not looking at. For ammonia diffusing into air from the data part of which we saw yesterday, let us say ammonia is component a and air is component b. Then we get D_{ab} at 1 atmosphere

and 25 degrees C to be 2.80 into 10 raise to minus 5 meters square per second and we have an expression for the molar flux of component a. In this case ammonia because it is a process of equi-molar counter diffusion; this will be minus D_{ab} divided R bar T p_{a2} minus p_{a1} by L.

Let us substitute - D_{ab} is 2.8 into 10 raise to minus 5 meters square per second, R bar will be 8314, the universal gas constant a 34 joules per kilogram mole Kelvin, 25 degree C is 298 Kelvin. In the second term, denominator is 1 meter; in the numerator we have the pressure difference; let us assume that there is no trace found of ammonia vapor in the atmosphere. The atmosphere is a large reservoir, whatever ammonia leaks in gets dispersed pretty fast; that is an assumption. So the partial pressure of ammonia in the surroundings that is effectively reservoir 2 will be 0; partial pressure of ammonia in the tank - it is full of ammonia, so it will be 1 but this is atmosphere so we will multiply it by 1.014 into 10 raise to 5 to convert it into pascal or newton per meter square.

Now, this gives us the value of the molar flux of ammonia is 1.146 into 10 raise to minus 6 kg mole of ammonia per meter square per second. We want to determine the leak rate in terms of kilogram per second of ammonia.

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So first, we calculate the molar flow diffusion rate of ammonia which will be the molar flux multiplied by area which will be pi by 4 into d squared; this turns out to be 0.225 into 10 raise to minus 10 kilogram mole of NH3 – ammonia - per second. And the mass flow rate of ammonia will be the molar flow rate multiplied by the molecular weight of ammonia which is 17. So this will be .225 into 10 raise to minus 10 multiplied by 17; the answer will be in kilogram of ammonia per second and this answer terms out to be 3.825 into 10 raise to minus 10 kilogram of ammonia per second.

Now, since it is an equimolar counter diffusion for air which is component b, we will have N dot b equal to minus N dot a - same magnitude opposite in direction. So the molar flux of air, flow rate of air, will be from right to left, so it will have negative value; this will be minus 0.225 into 10 raise to minus 10 kg mole of air per second. So the rate at which mass of air leaks in - I will not write the negative sign - will be .225 into 10 raise to minus 10 multiplied by the molecular weight of air, the equivalent molecular weight of air which is 209 and this turns out to be 6.525 into 10 raise to minus 10 kilogram of air per second.

After having obtained these 2 numbers, we should appreciate the magnitude of 2; notice 3.8 into10 raise to minus 10 kg per second of ammonia and 6.5 into 10 raise to minus 10 kg per second of air. The diffusion rates or the leak rates are pretty small; they are of the order of 10 raise to minus 10 seconds, that means even in 1 hour we will lose out something like10 raise to minus 6 of a kilogram,10 raise to minus 6 of a kilogram is 10 raise to minus 3 of gram that is of the order of 1 milligram in 1 hour and that means even if our tank contains ammonia of the order of a few kilograms, after 1 hour the amount of air into the tank is only going to be of the order of few milligrams of air. Similarly, the amount of ammonia which has leaked out will also be of the order of few milligrams of ammonia.

That takes care of our earlier assumption that during this process we have assumed the steady state and we have assumed that the pressure in the ammonia tank, temperature in the ammonia tanks and the concentration of ammonia in the ammonia tank does not

change. We have demonstrated by means of these numbers that it is a good assumption and even in 1 hour, the concentration of ammonia or the molar density of ammonia in the ammonia tank would have changed perhaps by 1 part in 10 raise to 6 which is one in million. Now it is time for us to move on to the next topic which is convective mass transfer.

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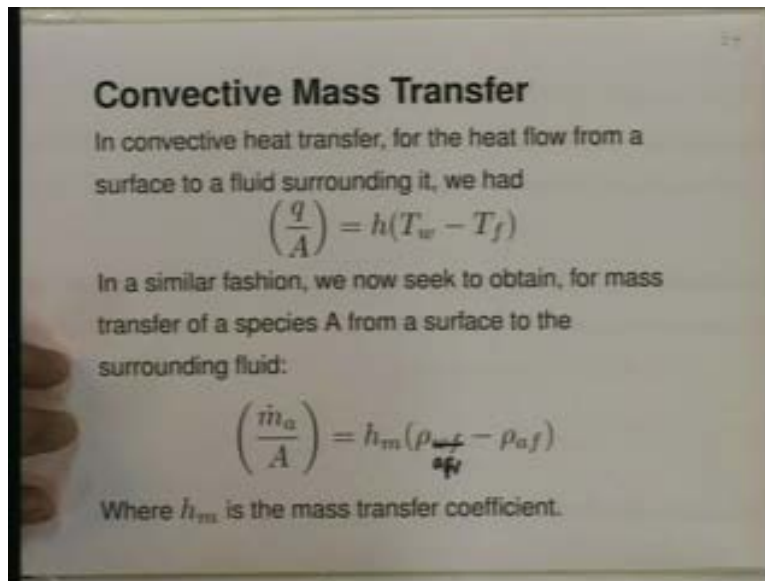
If we compare what we have done so far in mass transfer to the processes of heat transfer, you would have noticed that so far we have looked at situations which were similar or analogous to situations of heat conduction. Now, we move on to situations which are likely to be analogous to situations of convective heat transfer; so we now look at convective mass transfer. Since we have just studied heat transfer, it will be good to compare what we are trying to do with convective heat transfer.

In convective heat transfer for heat flow from a surface to a fluid surrounding it, we define a heat transfer coefficient such that the heat flux from the surface to the fluid surrounding it is represented it terms of the heat transfer coefficient multiplied by the temperature difference between the fluid between the wall and the fluid. In a similar fashion, in convective mass transfer, we assume that some species a is transported from a

surface to the surrounding fluid and we are interested in representing the mass flux kg per second of species A per unit area of the surface in terms of something similar to heat transfer coefficient called the mass transfer coefficient multiplied by the density difference between the wall and the fluid of the partial density of component a. Let me sketch the situation so that the ideas are clear.

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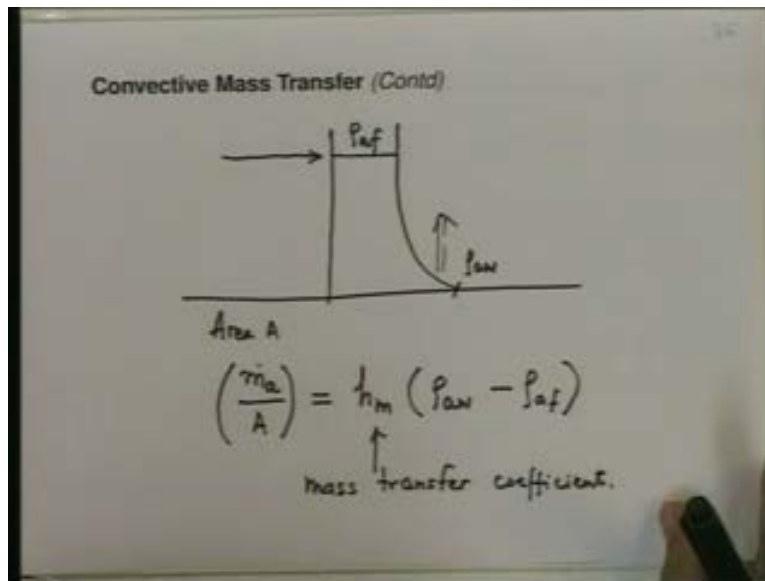
Let us say that we have some surface the area of the surface A; there is some fluid flowing and there is a component say A which is getting transported from the wall to the fluid. It is getting transported because if we plot the density difference for the fraction or component a, we will find that far away for the wall the density of component a, per kg of a per unit volume will be say rho af whereas at the wall it will be rho a wall. We want to write the mass flow rate per unit area in terms of the mass transfer coefficient multiplied the density of a at the wall minus the density of a in the free stream; this is the mass transfer coefficient.

Notice that in case of convective heat transfer if the wall is hotter, then the fluid heat transfer takes place from the wall to the fluid. If the fluid is hotter, then the wall heat transfer takes place from the fluid to the wall in convective mass transfer. If the density

of component a is higher near the wall as compared to that in the fluid, the mass transfer takes place from near the wall to the free stream away from the wall whereas if the density near the wall is lower than that in free stream, the mass transfer will take place from the free stream in to the wall. Again, it is possible that the mixture density rho is a constant if it is assume constant.

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Then we can write the basic relation defining relation for convective mass transfer in terms of the mass fraction of the fluid near the wall minus the mass fraction of the fluid in the ambient. Let us look at the units for the mass transfer coefficient. Notice that the mass fractions will be dimensionless; this is density so it will have units of kilogram per meter cube, this is mass flux so it will have units kg per second mass flow rate per meter square. So kg per second meters square or kg per meters square second since the equation has to be dimensionally homogeneous, h_n will have, there is kg common on either side. There is meter square in the denominator of either side so you will have here - the required units for h_m to be meters per second. It is interesting to note that the units for the mass transfer coefficient are also the units for speed or velocity.

When we talked about convective heat transfer we looked at the concept of a thermal boundary layer; now we look at a similar boundary layer for mass transfer.

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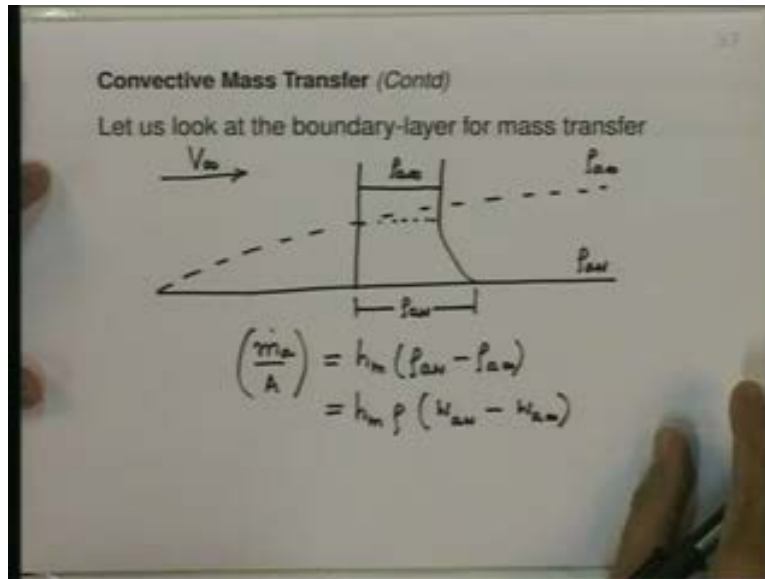
Let us say that we have a plate and on the plate we have a boundary layer, a velocity boundary layer with free stream velocity V infinity. Let us say that the plate is covered with some material, some fluid which diffuses into the free stream. Let us say that the component a has density rho aw near the wall and it has a density rho a infinity in the free stream. So, similar to the velocity boundary layer now, we will have a mass transfer boundary layer or diffusion boundary layer and if you plot the concentration profile, it will go like this - where away from the wall in the free stream the mass density of component a will be rho a infinity whereas just near the wall the mass density will be rho a.

Our aim is to write down the appropriate relations and obtain a relationship for h_m so that we can get finally, using this expression, h_m into rho aw minus rho a infinity or, assuming rho to be uniform in the boundary layer, h_m into rho into w a at the wall minus mass fraction of a in the free stream. We stop here now; we will continue with analyses of mass transfer boundary layers in the next lecture.