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Lecture No. # 02

We will like to sum up the lecture with the governing equation, which will form the basis to address the variety of diffusion problems. If you recall, we said total diffusion flux, total flux as absorbed by this stationary observer.

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NA will have two components; one is a bulk transport (()) write this flux same as V A C A, where V A is the molar velocity of the component A. This will also equal to x A N, the first component is bulk transport and the second component is a molecular diffusion. We can write x A, as which is mole fractions as C A over C A plus, and J A we can write as we defined earlier this is nothing but C A U A minus U bar. This is the molar flux of diffusion by Fick's law as absorbed by the observer, who is moving with this average bulk (()). This will equal to minus D A B del of C A over del of Z; so negative sign all it means diffusion takes place from higher concentration to lower concentration; C A 1 is greater than C A 2.

If you add it here this N A write substitute all these equations, this term becomes N A C A over C A plus C B. This is a term for mole fractions and we have N A, which is N A plus N B minus D A B del C A over del Z. We can box this equation as our governing equation for diffusion; you will see that this equation is a governing equation to address a several very common situations of diffusion in a stagnant or in equimolar counter diffusion cases. There are several such examples, which in which case, we can solve for a concentration profiles starting from this equation. The main idea is that N A has two components, one is the bulk transport, the first component, and the second component is your molecular diffusion by Fick's first law.

We would also like to revisit continuity or species balance, which you may have done in earlier lectures or earlier class or some other different course. Let us revisit species balance and continuity; also continuity is nothing but total material balance or total mass balance. What we do here is we will take a differential elements of del X del Y del Z or D B, and we will make a well known species balance, and we will see that how does it relate to what we have obtained just now.

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If you choose a control volume of del X of del V volume, which is del X into del Y del Z, and we assume there is a fluid flow of a binary mixtures of A plus B. We assume for our simplicity, it is a constant mass density or constant molar density fluid. So K G for cubic meter and moles for cubic meter, it is a constant we have A plus B; and if you

write down species balance if you recall we have del C A over del T plus del dot N A minus R A equal to zero. We have unsteady state now; we have total flux and if you recall this has two components; one was bulk transport and the second was diffusion flux; and this is a reaction tam. Essentially we are looking for moles in one cubic meter volume in one second, how does the moles changes? In one second, in one cubic meter of the control volume. And if we assume that there is no reaction, then R A equal to zero and we substitute N A from our previous equations which we had, where we said that N A has two components; one is the V C A bulk transport plus and the second component is your molecular diffusion.

If we substitute here we get del C A over del T plus V bar dot del C A equals D A B del square C A for del Z square. This is our species balance for A in this control volume of del X del Y and del Z. The first term is a unsteady state term and second term is your transport by convections by bulk transport and this term is your molecular diffusion term. This term can also be written if we write down the similar expressions, what we wrote or what we obtained just now that is a change in a concentration as absorbed by the stationary observer.

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But if the observer also moves with the bulk transport or with the average molar velocity, we have same term same equations written as D C A over D T equals D A B del square C A over del Z square. We have a substantial derivative; this is the rate of change in

concentration as seen by the observer moving with the average for the fluid average velocity.

So, this is again its consistent with what we had seen earlier that the observer, if you move with the bulk transport average velocity or he will see is the diffusion flux. On the other hand, if the observer is stationary you will see two terms here, one is with due to the bulk transport and one is with this molecular diffusion. We can also write down the similar balance for the component D B, which would be del C B by del T plus V dot del C B equals D A B del square C B over del Z square. And if you add the two equations, we get del C over del T plus V dot del C equals zero, because we have J A plus J B equal to zero. We are assuming that C bar is a constant.

If we write in terms of mass concentrations, we can write down same equation del rho over del T plus V dot del rho equal to zero, where we can substitute V with V star, where V star is mass average velocity. We define as very similar to how we define V bar or molar average velocity, it should be a rho A V A plus rho B V B over rho A plus rho B. This equation is well known continuity. We have obtained very simple equations for molar diffusion flux N A, and we have also obtained equations in terms of differential a control volume or differential species balance continuity as well. We will like to apply these different equations for different situations very simple well known, well used equations situations in case 1, case 2 and case 3 etcetera.

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We start with case one as an example, where we can apply the equations, which we have obtained. We are assuming steady state; we have binary mixtures of A plus B; there is no chemical reactions are equal to zero. We also assume the pressure and temperature is constant. So essentially, we are looking at Cartesian coordinates diffusion between one and two Z is the directions and A diffuses A and B, we have the diffusion for let us assume that there is a concentration gradient for A, and there is a concentration gradient for B. So under these conditions, if you assume that it is a steady state, there is no chemical reaction; all it means that molar diffusion flux of N A and N B, they are not function of time, and since there is no chemical reactions, and we have this cartesian coordinates, since per meter square of area. We have essentially, N A and N B they also do not change with set directions, because moles per second as well as moles per second per meter square are conserved in the Z directions.

We go back to our previous equations or what we obtained for N A in terms of bulk transport N A plus N B into mole fractions, which we can write as C A over C minus D A B del or D C A over D Z; so we are assuming 1 D diffusion flux. And this equation can also be arranged and integrate; since N A and N B they do not change along the Z directions, we can integrate from C A 1 to C A 2 between 1 and 2 with D C A over N A minus N A C excuse me minus C A N A plus N B equals one over C, D A B, D Z from Z 1 and Z 2.

We can integrate since C is a constant, N A N B diffusion flux are also constant, because of a steady state and as well as we are assuming that there is no reaction, so the molar flux is also constant at any plane between one and two. On the integration of this equation is not difficult to obtain an expression for N A in terms of the quantities like N B diffusion coefficients, Z distance between the 2 planes and concentrations. (Refer Slide Time: 12:17)

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It is very easy to obtain an expression for N A. A general expression for N A in terms of N A, we have N B D A B C over Z L and N A over N A plus N B minus C A 2 over C N A over N A plus N B minus C A 1 over C 2. This is a general expression, we have obtained for diffusion flux of A, but if you see it carefully, there is a term here N B. Even if these quantities like diffusion coefficients D A B, C which equals P over R T Z diffusion length the unknown, and we know the concentrations at the two planes C A 1 and C 2, we cannot solve for N A in terms of these quantities, because N B is also known, which means we must look for relation between N A and N B.

All it means that we have to take some special cases, in which we can have one more independent equation to solve for it. One of the examples would be that if you have the same one in planes for A to diffuse in that Z directions. If you assume that, A is getting decomposed into B and some other components. So we can take an example of say methane, which is A decomposes into carbon and hydrogen; so the surface is acting as a catalyst. In other words, there is no homogeneous reaction inside these two planes; so R A is stills zero, but when A reaches the plane two it gets decomposed by some catalytic reactions into carbon and hydrogen and hydrogen diffuses in the opposite directions.

In this case, if you look at the stoichiometries, if we recall we said that one of the prerequisite is stoichiometry. In this case, we can say that N A and N B they are related with due to their stoichiometric ratios. We have one more equation essentially, N B in

terms of N A. We can go back and substitute N B in terms of N A to obtain a relation for molar diffusion flux of A in terms of all the unknown quantities, which we have.

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If N B equals minus 2 of N A then we can write N A over N A plus N B equals minus 1; and therefore we have an relation for N A minus D A B C over Z ln 1 plus Y A 2 over 1 plus Y. We are trying to say here that we have obtained a relations for a special case, in which we can predict how much is this molar moles per second per meter square of your diffusion plane in terms of diffusion coefficients bulk total concentrations Z and mole fractions of 1 and mole fractions of A at planes 1 and 2. The mole fractions Y will be the same as C A over total concentrations or if it is a gas we can write in terms of partial pressure of A and the total pressure. So all we have done that we have obtained this relation for N A in terms of the unknown quantities.

We will take another example case 2 in which case, we have a steady state diffusion of A through stagnant B. So what we say is that stagnant B, we have N B equals zero, and a very common example would be if you have water and air and ammonia, so we can assume that air is insoluble in water and ammonia is soluble. It will diffuse, and will get solubilized in water. We also assume that water does not evaporate for hours (()). There is no chemical reactions R equal to zero. We assume steady state all the diffusion flux, which we have N A and N B, they do not change with time now do they change with Z, so we can have the access here with Z from zero to some high, so all we will do now. We

will go back to the same equations start from the governing equation, which we obtain here and we try to see how we can simplify it.



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So if we go back to the same equations N A equals mole fractions X A, N A plus N B, but N B is zero, because air is stagnant minus D A B, D C A over and X A, we can write in terms of partial pressure of A and the total pressures. So we have P A by P A, N A minus D A B by R T, you can apply ideal gas law to make it D P A over d z. We have said C A equals concentration of A equal to p A over R T applying ideal gas law; and P you can write as sum of two partial pressures P A plus P B.

So now we have obtained relation between N A and this partial pressure gradient; since steady state N A does not change with time nor N A changes along the direction of Z. There is no chemical reaction here; so we can easily integrate these equations, which is independent of Z to obtain N A equal to D A B, p T over R T Z, ln P T minus P A 2 over P T minus P.

In this case 2, when B is a stagnant we have obtained the relation for diffusion flux of N A in terms of the known quantities partial pressure of A at 1 and 2 and the diffusion there. More important here is to understand how do the profile will change between the two planes. So look at this, if we have this water and air interface it is ammonia, which is diffuses inside. So ammonia is soluble, and this will have a concentration gradient for ammonia to diffuse air, but air is insoluble; air is insoluble and one can also write down

express N A and N B both in terms of molar diffusion flux as well as the bulk transport. Important here please note that since air is insoluble in water, there is bulk molar convections or bulk molar transport, induced because of ammonia diffusion. Since N B is zero which means V C B, so the bulk transport of B of air has to be equal to the molar diffusion flux of air. In other words, any stationary observer he will observe that B is 0, but if this guy moves with this average velocity of with U bar he will see that there is a diffusion flux given by D A B and D C B. This principle of one medium diffusing, when the other component is stagnant is applied very frequently in case of way so-called example known as Stefan tube.

So we did here that we started with the same equations and we solve for case 2, where we say that A is diffusing, but B is a stagnant, N B is 0. So when we say that B is a stagnant total molar flux of B is 0 that does not mean that B does not have if an observer moves with this convective or B velocity, he will see air diffusion by this Fick's first law, but to the extent that molar diffusion flux of B will be counter balanced by the bulk transport. So, this principle is very frequently applied in obtaining or predicted the diffusion coefficients in well known Stefan tube.



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So, we will take this example of Stefan tube, which is very simple tube, geometry configurations to measure or to predict binary diffusion coefficient. Essentially, we have a U tube, and say we want to measure or we want to predict or estimate vapour of an

organic compound say acetone in air, so we have a tube like this, in which air moves very gently on top of this. So, when the acetone evaporates, it has a diffusion length of del Z or some height H, before it is carried by this air is steam ports.

We can assume that air quantities are very large to the extent that the concentration of acetone C A 2 is 0, a mole fraction of two is 0 at this location. At location one, the interface of acetone and air, we can write Y mole fractions of A at location one A is here is acetone, as vapor pressure at that temperature and the total pressure is zero over P. So we assume that air is not soluble in this quantity, and with this technique one can obtain this you can predict the diffusion coefficients of acetone in air. If you look at carefully as acetone evaporates, its level is going to come down; so if you start with this locations at some location t equal to 0 after sometime acetone will evaporate, and this level will get down to some level t equal to t 1 one from Z 1 to Z 2.

In other words it is unsteady state problem, because the level of acetone continuously keeps on decreasing. If the level of acetone decreases or Z like if we put the axis here, if z decreases from some level Z 1 to Z 1 it is unsteady state problem, and we cannot apply what we obtained for diffusion flux of A in terms of your bulk transport, and your molar diffusion flux, because every time in all the two cases, which we had earlier we assume that N A it is a steady state, N A does not change with time and N A does not change along the Z directions. Since the level of acetone change decreases it is a unsteady state, but is still the more important also here to notice that the level of this acetone decreases very slowly. In others word we can assume what do we call pseudo steady state approximations, which means or this also known as quasi steady state approximations.

In other words, in this case, since the level of acetone decreases very slowly, so we can assume that over the time period of diffusion flux, the level of acetone is almost constant that is the pseudo steady state approximation. In chemical engineering or in so many contexts, you will be seeing that we make this kind of approximations. Whenever we have two rates and one rate is much larger than the other rate, one can as applied this quasi steady state. Here level of acetone decreases very slowly may be when you do this experiment, in your lab, you will see that it takes almost 8 to 10 hours and if not 24 hours before you see a measurable difference in the height.

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Assuming that it is a quasi steady state, we can still apply the pervious equations air is insoluble, so we can say that N B which is air is 0, and you can apply the previous equations directly there NA which we wrote as D A B P T over R T Z l n P T minus partial pressure of A allocations 2 over P T minus P A 1. P A 1 as we said that P A 2 (()) be zero, because as soon as the acetone gets into this stream, we can assume that it strip by this air. Partial pressure of A 1 you can write as vapour pressure or acetone at this temperature. This is the equation except that which should be able to make a material balance assume that the level decreases from Z 1 to Z 2 over a time period of T. If N A is the diffusion flux or N A into cross sectional area, so this would be the cross sectional area into del T, this will become your moles so over del T, so much moles of A has diffuse; and this is nothing but how much material has evaporated. So we have del Z, into cross sectional area that will make it volume into rho that density divide by M A.

We have made a material balance and we can substitute this N A here, we can integrate now, this D Z over this del Z to obtain this relations D A B, R T if it suggests simple substitution P T over Z ln P T P A 2 we can assume 0 P T minus vapor pressure equal to rho A over M A we have d Z over d T. We take the limit del T tends to 0. We have obtained this relation; we substituted N A from here and now we can integrate d Z and d t to obtain or to predict diffusion coefficients in terms of all known quantities, which is rho A over M A, R T over P T, we have l n P T minus P A 1 over P T minus P A 2 Z 2 square minus Z 1 is square over two into one over total time. So we have this d t integrate this term. So, knowing all this quantities actually we said that P 1 is 0, so we can delete this term we have P T minus is 0.

So now one can get an estimate of diffusion coefficients of acetone in air. So All this Stefan diffusion you made an approximation on that there is quasi steady state and the rate of fall of acetone vapour in air in the tube is very small, so N A and N B both of them remained constant with the time as well as along this length Z, and then we integrated equations to obtain quantities for diffusion coefficients, which we can be obtain in quantities meter square per second for acetone in air.

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We will take one more example to apply what we have done in earlier, so this would be the case 3, and this is simple example, but it is called steady state. We have steady state equimolar counter diffusion and in other words, we have N A equals minus N B, which is a constant at time in other words N equal to 0, there is no bulk transport. And if you put the same equation of N equal to 0 and simplify we have N A equals minus D A B over R T D, p A over Z, and then one can integrate (()) expression for N A equals D A B, R T Z, p A 1 minus p A 2.

Essentially, we have a total pressure here we are saying that p T is constant and there is a gradient of p A from p A 1 to p A 2, and there is a gradient of B from p B 2 to p B 1 and total pressure p is some of the two case partial pressure p A and p B. These are the examples, which we took three examples case 1, case 2 case 3 where we have shown that

we can solve for diffusion flux or we can predict the diffusion flux. And one of the example we had applied in case of Stefan tube, which is widely use to predict or estimate diffusion coefficients of one species, vapour species diffusing in other species like D A B etcetera.



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If you look at carefully this equations Fick's first law, we wrote J A equals minus D A B D C over D Z, so this unit of J A is moles per second per meter square, C A is moles per cubic meter and we have meter square per second. Of course, they are experimental measure methods to measure D A B or they are so many models, to predict this D A B in general for gases one correlation is quite very popular given by Wilke and Lee, which we must know at least that diffusivity, binary diffusivity is proportional to one over M A plus one over M B, only depends upon all it means that lighter molecules will have larger diffusivity and heavier molecules will have smaller diffusivity. It is a temperature dependent to the power 3 by 2 1 over total pressures and also depends upon on the size of the molecules. In other words, R A B is nothing but the average radius of two molecules of R A and R B. So at least we should remember that it has a strong temperature dependence e to the power 3 by 2 and it is one over pressures.

Diffusion for liquids are so many correlations available to estimate, for the liquids the one for dilute solutions, we should know that zero signifies for a dilute liquids solutions. It is a molecular way to the power half T over viscosity. Here it is T to the power 3 by 2

for the liquids; it is linearly proportional to temperatures. And whatever equations we obtained for the gases, we can equally write for the liquids except instead of partial pressure, which we use for the gases we can write in terms of concentrations.

CA = 14/2T , NA = CA/G+B $\overline{C} = \left(\frac{P}{H}\right)_{avg.}$ $\frac{Case 3}{2}$ $\frac{Case 3}{N_A} = \frac{DAB}{2} \left(\frac{C_H}{H} - \frac{C_{AD}}{2}\right)$ $= \frac{DAB}{2} \left(\frac{P}{M}\right)_{avg.} \left(\frac{N_{AH}}{H} - \frac{N_{AD}}{2}\right)$

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In other words, we can write C A as P A over R T and mole fractions we can write as C A over C A plus C B; so for the liquid, we use the nomenclatures X A and for the gas we use X B. Total average liquid concentration or solution concentration can also be written as C equal to rho over M average density. We just take the case 3 for our simplicity, if you want obtain the similar expression for the case of liquid and we can write N A as D A B over Z as C A 1 minus C A 2. Instead of partial pressure of A and 2 of A at 1 in 2 for gases substituting with the concentration of C A Z minus C A Z. And also write this as D A B over Z, and rho by M as average concentrations liquid concentrations and we can write in terms of mole fractions of A in liquids in that location 1 and 2. Similarly equation can be obtained for all this two cases, which we did earlier case 1, case 2, and case 3.

Now before we end this lecture, we should also what we did obtained so far for those cases of 1, 2, and 3 we had rectangular coordinates in which case when A or B diffuses, then the planes are rectangular planes, and area of this plane they do not change with the distance Z. But we can have several common examples of this spherical geometries or cylindrical geometries, where the area changes as you go along this R direction. We have

4 pi R 1 square 4 pi R 2 square or in case of cylinder we will have 2 pi R 1 L and 2 pi R 2 L.

So in these cases, what happens? When we say that there is a steady state it is moles per second, which is constant; moles per second per meter square of the diffusion plane will change. Unlike in case of the cartesian coordinates, and we say that is a steady state moles per second as well as moles per second per meter square both are constant. So, we have to do is that go back and start with the same equations for N A in terms of bulk transport diffusion flux except, when we integrate we have to be careful that area changes in terms of R and it is a moles per second, which is constant not moles per second per meter square. It is a very common example in case of evaporation of a naphthalene ball. If you have a naphthalene ball or some casper spherical ball, and if it evaporates in a stagnant air its size will change with time. The way we have seen in case of Stefan tubes.

We took the Stefan tubes, we had the surface of acetone when it evaporates the level of acetone decreases, but still we have cartesian coordinate system cross sectional area does not change the time, but in case of a spherical ball or like naphthalene ball we said when it evaporate, the size will change or when A evaporates into stagnant medium, then we are encountering different planes of different radius.

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We will take this example for spherical geometries. Essentially now we have diffusion in spherical coordinate. We have similar sections it is a steady state, there is no reaction so when we say steady state actually it is a moles per second, which is constant. We have saying that steady the state N A and N B both will be functional of R origin, although it is a steady state; why because if we look at different planes, then we have A diffuses like this on the surface area or the diffusion plane area will change from four pi R1 square to four pi R2 square.

In other words N A, which is moles per second per meter square into 4 pi R square this will be constant so what is constant here in case of spherical coordinate is moles per second and not moles per second per meter square. Similarly, if you have cylindrical coordinates then we are trying to say that is N A into 2 by R that is a constant. In case of this is a cylindrical coordinates and if we have Cartesian coordinates, which we did earlier it is N A which is constant. It is very important that we may understand that it is a moles per second or multiply by the density and kg per second is consumed, not moles per second per meter square.

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$$\begin{aligned} \begin{split} & \mathcal{A} = \frac{|\mathcal{F}|_{\mathcal{S}}}{|\mathcal{S}|_{\mathcal{S}}} = \frac{N_{A} \times 4\pi \Upsilon^{L} \star f_{A}}{R_{I} \leq \Upsilon \leq k_{L}} \\ & \mathcal{K}_{I} \leq \Upsilon \leq k_{L} \\ & \mathcal{M}_{A} \begin{pmatrix} \Upsilon \end{pmatrix} = \frac{1}{2A}N - \frac{1}{2A}\frac{d(A}{dT} & N_{A} \neq \frac{4\pi \Psi}{dT} \\ & \mathcal{M}_{A} \begin{pmatrix} \Upsilon \end{pmatrix} = \frac{1}{2A}N - \frac{1}{2A}\frac{d(A}{dT} & N_{A} \neq \frac{4\pi \Psi}{dT} \\ & \mathcal{M}_{A} \begin{pmatrix} \Upsilon \end{pmatrix} = \frac{1}{2A}N + \frac{1}{2A}\frac{d(A}{dT} & N_{A} \neq \frac{4\pi \Psi}{dT} \\ & \mathcal{M}_{A} \begin{pmatrix} \Psi - \Psi_{A} \end{pmatrix} = \frac{1}{2A}\frac{d(A}{dT} & \mathcal{M}_{A} \end{pmatrix} \\ & \mathcal{M}_{A} \begin{pmatrix} \Psi - \Psi_{A} \end{pmatrix} = -\frac{1}{RT}\frac{dA}{dT} & \mathcal{M}_{A} \end{pmatrix} \end{aligned}$$

So, now we take the same similar expressions and we substitute in the previously, what we have obtained in case of any in terms of bulk transport and diffusion flux. We say that W A if we defined a quantities which is kg per second then this is N A into 4 pi R square into rho A, where rho is a density and R varies between R2 and R1. And We have

the expressions for N A, now it is a function of R or Z equals mole fractions y A into N minus D diffusivity D C A over D R. It is same expression except we realize that N A is a function of R, and N A although it is a function of steady state, it is not a function of time, but N A changes with R.

We have W dot R, N A 4 pi R square into rho A and we are starting from the same equation, which we had earlier N A r equal to Y in bulk transport in this diffusion flux. We substitute here or we multiply this equations with 4 pi R square into N A equals 4 pi R square Y A N A equals N A plus N B minus D C A over D R. If you go back to the same case, where we say that N B is zero, in very special case, which we had earlier that diffusion medium A diffuses, but B is a stagnant.

There is a similar case except now we are in the spherical coordinates, and we have a steady state, so kg per second is conserved N A into 4 pi R square and W is constant. Now, we can substitute and we make it N B equal to zero, we can substitute this equation here to obtain W dot P minus over P equals minus D over R T D P A over D R 4 pi R square all we have done. We have made N B equal to zero and we have substitute 4 pi R square N A has W dot and W dot is constant is a kg per second; it is conserved here equal to minus 4 pi R square. Now we can integrate.



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If we integrate W dot R T over 4 pi P D A B integration from R 1 to R 2 D R over R square equal to P A 1 P A 2 D P A over P minus P A. This small p is same as a partial

pressure, so let us use on the same nomenclature D P A P minus P A. Essentially, we are integrating from R 1 to R 2, which is N A and we realize that at any location R the diffusion area is 4 pi R square, which varies from four pi R 1 square 4 pi R 1 R 2 square. We have partial pressures P A 1 and P A 2. So now, we can integrate to obtain equations for W dot R T 4 pi P D A B 1 over R 1 minus 1 over R 2 equals 1 n total pressure minus P A 2 over P minus P A.

So just an example, which we have taken here for diffusion of A in stagnant B, where we have a spherical coordinates. It is a very similar to a naphthalene ball, we have sphere, and this sphere evaporates in air which is a stagnant. And if you compare what we had earlier, we had a Stefan tube filled with acetone and acetone evaporates. In this case when the acetone evaporates, then all the diffusion area is a constant. In case of naphthalene ball or naphthalene vapor, when it diffuses the air and area changes from 4 pi R 1 square to four pi R 2 square etcetera.

In which case, it is a moles per second, which is conserved not moles per second per meter square in case of spherical coordinates. Unlike in the cartesian coordinates both moles per second and moles per second per meter square is conserved. These are the three examples, we have taken in today's lecture case 1, case 2, case 3 mostly for cartesian coordinates, and one example we have seen for spherical coordinates.