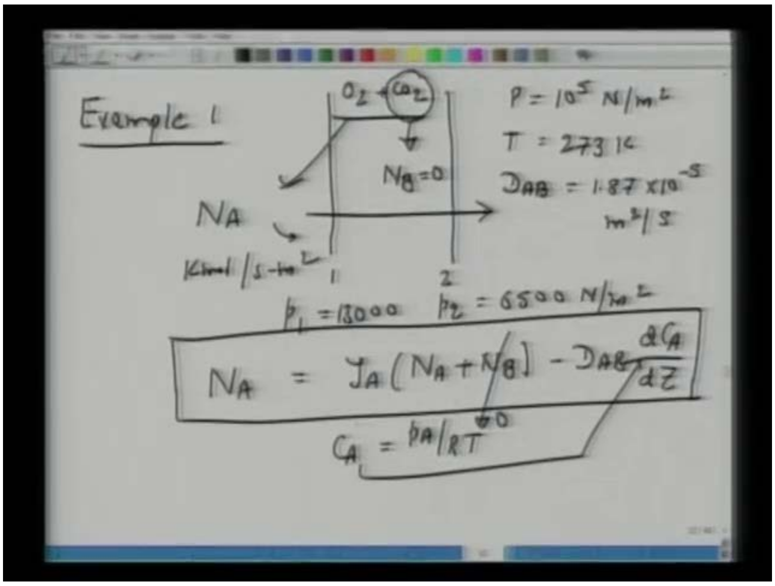
Mass Transfer II
Prof. Nishith Verma
Department of Chemical Engineering
Indian Institute of Technology, Kanpur

Lecture No. # 03

So, in today’s lecture, we will take a few examples based on what we did in our previous couple of lectures, that is the basic principle of Mass Transfer. So, if you recall, we derived a general expression for mass transfer by diffusion. So, essentially, we had two terms for the molar flux: one was by the bulk transport from one location to another, and the second was term due to fix diffusion, that is the molecular diffusion as observed by the absorber, who is this who is moving with the bulk velocity, and we also did define the bulk average velocity of the fluid.

So, we had two special cases: one was when the fluid medium is a stagnant, and the second one we had when we have equimolar counter diffusion, and we said j equals minus j b or if… So based on that, we simplified N equal to minus N B, and then, we simplified the expression for molar diffusion flux. We integrated and we got the expressions for N A, N B etcetera. So, we take a few examples, introduce the lecture, couple of examples that will essentially elaborate.

(Refer Slide Time: 01:33)



$P = 10^5$ N/m^2

$T = 273$ K

$D_{AB} = 1.87 \times 10^{-5}$ m^2/s

$p_1 = 13000$ $p_2 = 6500$ N/m^2

$$\boxed{N_A = y_A(N_A + \cancel{N_B}) - D_{AB}\frac{dC_A}{dZ}}$$

0

$C_A = p_A/RT$

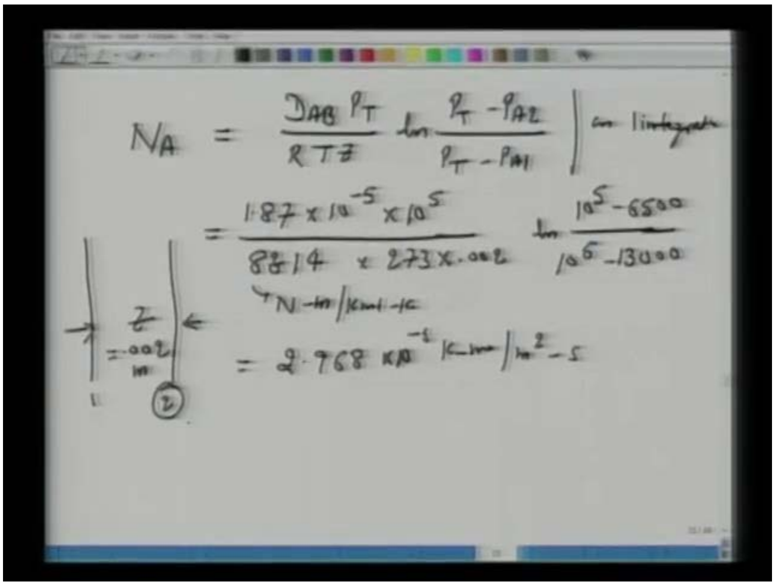
So, let us take this example 1. So, what we have here? We have a two planes, say 1 and 2, binary mixture of oxygen and carbon dioxide; let us assume the pressure is given 1 atmosphere, 10 to power 5 newton meter square, and we have temperature 0 degree Celsius or 273 Kelvin; and also given that binary diffusivity of A and B are oxygen and CO 2, it is 1.787 10 power minus 5 meter square per second.

The question here is that, one this carbon dioxide CO 2, say it is a stagnant; so, when we say, CO 2 is a stagnant or non diffusing, essentially we are saying that N B equal to 0; and the question is, due to a concentration gradient or partial pressure at plane 1, 1300 13000, and at plane 2, P 2 equals 6500 newton per meter square; we are interested in finding this diffusion flux of N A, in terms of say kilo mole per second per meter square.

So, it is a very simple example, the first one to start with. And we start with our expressions for N A, which we developed in our earlier class. So, we have y A; N A equals y A, N which is N A plus N B minus D AB d CA over d Z. So, this was our first governing equations for diffusion flux. Since N B is 0, we have simplified expressions; we can always convert, write C A in terms of partial pressure as P A over R T. So, this C A can be substituted, and one can integrate these equations; the idea is that either you start from here or idea is that either you start from here or you start from the integrated equation, which we had plot and we had simplified earlier.

So, we go back to our previous expressions, when we are integrated between 1 and 2 and obtained the relations for diffusion flux.

(Refer Slide Time: 03:50)



$$N_A = \frac{D_{AB} P_T}{R T Z} \ln \frac{P_T - P_{A2}}{P_T - P_{A1}} \Bigg|$$ on integration

$$= \frac{1.87 \times 10^{-5} \times 10^{5}}{8314 \times 273 \times .002} \ln \frac{10^{5} - 6500}{10^{5} - 13000}$$

↳ N-m/kmol-K

$$= 2.968 \times 10^{-5}$$ kmol/m^2-s

So on integration, one can show that you will get N A D AB total pressure R T Z ln P T minus P A2 over P T minus P A1.

So, this is on integrations, which we did in the previous lecture, and we can a start from here also. So, all we have to do is right now is to substitute all the values for whatever numerical values we had here, which is 1.87 10 to power minus 5 for diffusivity total pressure 1 atmosphere 10 power 5 gas constant R 8314; so, this unit would be a newton meter per kilo mole Kelvin, temperature is given 0 degree Celsius or 273 Kelvin, and we had this diffusion length, the distance between the two plane at Z between 1 and 2 as 2 millimeter, which is 0.002 meter. So, this 0.002 into ln P T is a total pressures 10 to power 5 minus partial pressure at location two, which was given as 6500, total pressure 10 to power 5, and we have partial pressure at 1, which was given as 13000. So, all we have to do is the substitution, and solve to obtain 2.968 10 to power minus 5 kilo mole per meter square per second.

So essentially, if this example is a most simplest example, in which case, we have assume that the bulk medium are N A plus of N B, in which any diffusions is a stagnant. So, we had N B is equal to 0, and we substituted, we have two components, then we integrate to obtain this simplified expression for diffusion flux.

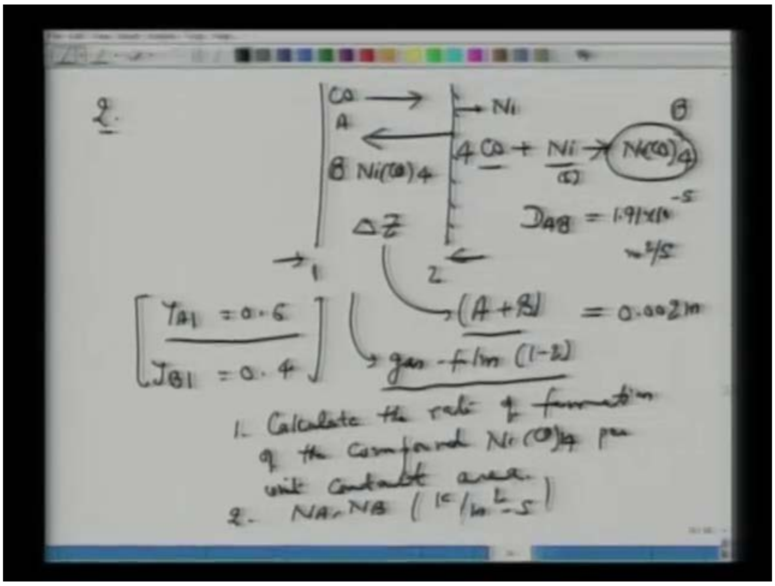
We will take slightly more complete complex examples, in which in the same plane 1 and 2, any diffuses, and then, when it reaches the second plane, there we assume that it is a, there is a heterogeneous chemical reactions.

So, A gets converted say, into B, and then B diffuses back to this this diffusion medium. So essentially, still we have binary mixture of A plus B; now if you recall what we did in the previous previous classes, previous lectures, we made certain assumptions; we said that first steady state.

So, whatever expression we used that time and even today's in the first example, we had a steady state; that is what, number 2 we said that there is no chemical reactions, which means, the plane we are considering - the diffusion plane of 1 and 2, there is no chemical reactions; in this example, we will see that there is a chemical reaction at the surface, that is alright; still we can use the expressions, which we obtain for a steady state and no chemical reactions.

So, this example 2 is a very simple is a simple example, but still, a slightly different from what we did in the minutes ago.

(Refer Slide Time: 06:55)



$4CO + \underset{(s)}{Ni} \rightarrow \boxed{Ni(CO)_4}$

$D_{AB} = 1.91 \times 10^{-5}\ m^2/s$

$= 0.002\ m$

$y_{A1} = 0.6$

$y_{B1} = 0.4$

1. Calculate the rate of formation of the compound $Ni(CO)_4$ per unit contact area.
2. N_A, N_B $(k/m^2 - s)$

So, let us get back to this example 2, where we have two diffusion planes 1 and 2, and now we have carbon monoxide, which diffuses in this directions; concentration of carbon monoxide here it is given, it is 60 percent.

So, we say that y A1 is - carbon monoxide is mole fraction is 0.6 and when carbon monoxide reaches plane 2, then there is a reaction.

So, we can assume that, it is a heterogeneous surface, which is say coated with nickel. So, what we have CO plus nickel giving to nickel carbonyl CO 4. So, you balance this 4 CO plus nickel. Now, this product of nickels carbonyl, this also diffuses back into this. So, we have now, B of nickel carbonyl; so, the more important here to understand that we have binary mixture of A and B, carbon monoxide diffusing from 1 to 2, and the product diffuses back into this bulk mixture of A and B.

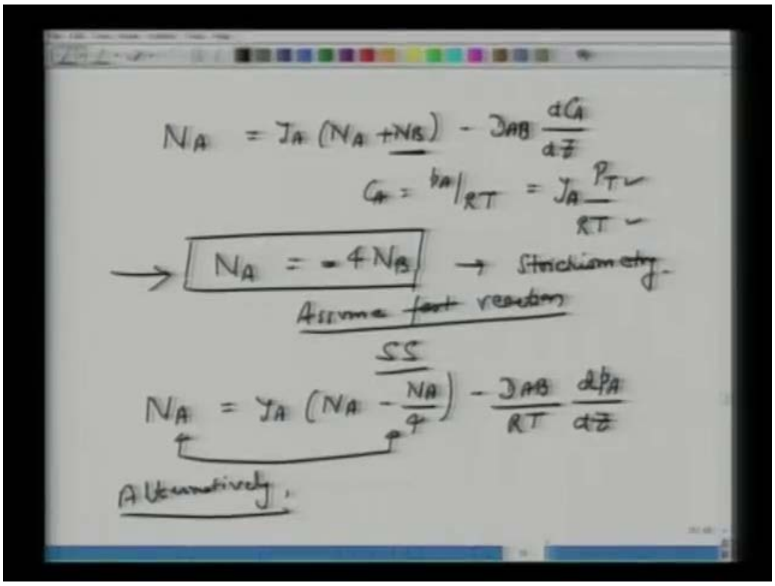
There is a chemical reaction, but the reaction takes place at the plane 2, that is more important. So, in this A and 2 , between 1 and 2 this diffusion medium of del z, there is no chemical reactions; you can still assume a steady state, no chemical reaction and apply the same expression, which we obtain earlier; although the reaction takes place at the boundary, not within the homogenous system.

So, now we go back and we apply the physical properties of all these - the system is given D AB of carbon monoxide in nickel carbonyl or nickel carbonyl in carbon monoxide, is given as 1.9110 to power minus 5 meter square per second. This gas film, if you call it and this binary mixture of gas film between 1 and 2 alright; del z is given as 2 millimeter, which is 0.002 meter. Now, the concentration of 1A is at the location 1 in the bulk medium is given point 6, and there x is y B1, which would be 0.4.

Now, if you notice here that A diffuses in this directions, and B diffuses in the reverse directions, and if you go back the stoichiometries, we have 4 molecules of carbon monoxide reacting with one at the surface; this nickel is at the surface to give back this product B in the stoichiometric diffuse of 4 is to 1.

So the question is, number 1 - first question is, calculate the rate of formation of the compound, which is here nickel, carbonyl CO 4 per unit contact area. So, this contact area is nothing but the plane 2; before this or we can also calculate the flux of NA and NB, you will see the all of this is well related to each other; before we make any other assumptions or restrictions, let us try to… Let us start with the same expression, which we obtain for molar diffusion flux of A and B.

(Refer Slide Time: 10:40)



$$N_A = y_A(N_A + \underline{N_B}) - D_{AB}\frac{dC_A}{dz}$$

$$C_A = p_A/RT = y_A\frac{P_T}{RT}$$

$$\rightarrow \boxed{N_A = -4N_B} \rightarrow \text{Stoichiometry.}$$

Assume fast reaction

SS

$$N_A = y_A\left(N_A - \frac{N_A}{4}\right) - \frac{D_{AB}}{RT}\frac{dp_A}{dz}$$

Alternatively,

So, we start with the same expressions, what we had N A equal to y A N A plus N B minus D AB d CA over d Z. Since with the gaseous mixture, it is not a bad idea to convert this C A into the partial pressure P A by R T, and we can also write this as a mole fraction y A total pressure over R T.

Now, the question is that we are trying to solve N A, and we have one more unknown which is N B; in the previous example, if we recall, we had stagnant B. So, we could substitute N B is equal 0; here, we have N A diffusing in one directions, and N B diffusing in the opposite directions. So, both are unknowns; both we are suppose to calculate. So, all it means that we are looking for one more expressions or one more equations to make the problem well defined.

Now, if you one has to go back to the stoichiometry, to see that one molecule of nickel reacts with 4 molecules of carbon monoxide, to form this product B, which is nickel carbonyl; that means, we can apply the stoichiometry here. So, if you apply the stoichiometries, then you will should obtain N A equals minus 4 N B. So, when we write these expressions, there is of course, a stoichiometry involved; but more important here is that, if you recall in our… On a previous lectures, everywhere, we are assuming that we have a steady state; that means, concentrations anywhere between 1 and 2 does not change with time.

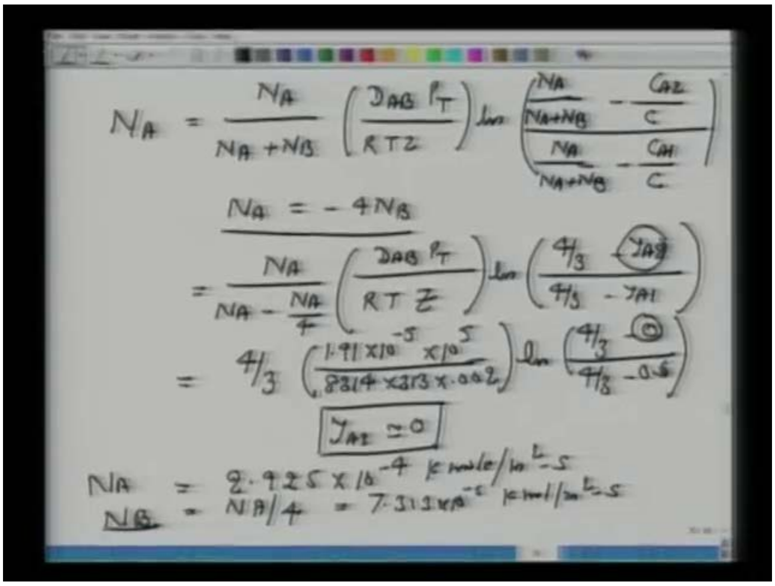
Now look at very carefully, the two rates here: one is the rate of diffusion of A and B, and the second is the rate of chemical reactions at the surface. So, when A arrives, there is a rate - finite rate, at which A gets converted into B, and then this B has to be diffused back. So, when we assume steady state, again we have to qualify by saying that reaction A to B is very fast; in other words it is not a rate limiting, and what is limited here is, still is by diffusing; then we can write N A equal to minus 4 N B by stoichiometries, and we say that assume steady state or assume fast reactions.

So that, we can assume steady state; it is also a quasi steady state approximations; because they are two rates: one is a rate of diffusion, and the other is the rate of reactions; we are assuming that the reaction is very fast as soon as A arrives, it is form into B and B diffuse back. So, still we are looking at between medium 1 and 2, where we have a steady state and there is a reaction at the boundary, which is very, very fast. So with that restrictions, we write N A equal to minus 4 N B of course, we bring the stoichiometry; and then we solve this equations.

So now, once we assume N A equal to minus 4 N B or we have to do is to substitute in the previous equations, N A equal to y A N A and N B is N A over 4 the minus sign signifies, here the diffusion flux is in the opposite directions minus D AB we go back and substitute P T R T etcetera to make it D AB over R T we have d PA over d z.

Now, we can integrate and solve for this, in a molar diffusion flux of N A, which we did it in the previous class; so the idea here is, not necessity every time, you have to go back, and start from the principle, we can also start from alternatively, you can start from integrated equations, and in that equation you can… You can substitute N A equal to minus 4 N B. So, we like to go back to the previous equation, which was integrated in terms of… For N A in terms of N A, N B it was implicit of course, in terms of concentrations; but in that equation also, we can substitute this stoichiometry, and then, we can solve the problem.

(Refer Slide Time: 15:04)



$$N_A = \frac{N_A}{N_A + N_B}\left(\frac{D_{AB} P_T}{RTZ}\right) \ln\left(\frac{\frac{N_A}{N_A+N_B} - \frac{C_{A2}}{C}}{\frac{N_A}{N_A+N_B} - \frac{C_{A1}}{C}}\right)$$

$$\underline{N_A = -4N_B}$$

$$= \frac{N_A}{N_A - \frac{N_A}{4}}\left(\frac{D_{AB} P_T}{RTZ}\right) \ln\left(\frac{4/3 - y_{A2}}{4/3 - y_{A1}}\right)$$

$$= 4/3\left(\frac{1.91\times10^{-5} \times 10^{5}}{8314\times313\times.002}\right) \ln\left(\frac{4/3 - 0}{4/3 - 0.6}\right)$$

$$\boxed{y_{A2} \simeq 0}$$

$$N_A = 2.925\times10^{-4}\ \text{kmole/m}^2\text{-s}$$

$$\underline{N_B} = N_A/4 = 7.313\times10^{-5}\ \text{kmol/m}^2\text{-s}$$

So, let us go back to the integrated equations, which we had earlier of N as N A equal to N A plus N B D AB c by z. So, instead of C we write P T over R T Z l n N A over N A plus N B minus Co 2 over C N A over N A plus N B minus C A1 over C. So, this the integrated equations; we can start from here, if we remember or we can go back to the original equations for N A1 expressing governing equations, and then we can integrate after substituting that N A equal to minus 4 N A, either way it will work. So this, we should try as an exercise, both phase, you know, so that into you realize that you have not made any mistake in this numerical integrations.

Now, we can substitute N A equals minus 4 N B in this integrated equations, then we have N A over N A N B if you remove we have N A over 4 D AB P T over R T Z l n N A over N A plus N B if you substitute we have now 4 by 3 C A T by C is nothing but the mole fractions at location 2 and we have 4 by 3 minus y A 1.

So, we have N A over N A minus 4 N A by 4 to make it 4 by 3 D AB 1.91 10 to power minus 5 total pressure 10 to power 5 or 8314 same SI unit temperature 313 Kelvin diffusal length 0.00 l n 4 by 3 minus 0 over 4 by 3 minus 0.6. So, let us make a note here also, we are assuming y A T equal to 0 or approximately 0, and here as you said earlier, there is a restrictions, why we are assuming why a, why mole fractions of A at the surface, at let it surface 0, and the reason is only one that it is a very, very fast reactions as soon as A arrives, it is getting converted into B. So, the mole fractions of y at the surface is 0; all this different, different assumptions, which we are making is quite important, that we note and when we apply an expressions, we try to realize that at what point, at what step we are made those assumptions; a steady state alright when we say is the steady state, we must ensure that all the other rates, if they are there, their act quasi steady state are very fast.

So here, we have two rates: one is the chemical reaction rate, and one is the diffusion rate; chemical reaction rate is very fast, then only you are making this a steady state assumptions; mole fraction of 2 of A at the location 2, 0; why? Because it is a very fast reactions, N A equals minus 4 N B; why? Because there is a stoichiometries, the moles of 1 mole 4 molecules of carbonyl, CO carbon monoxide gives 1 mole of products been.

So with that restriction, we have simplified these expressions, and we have obtained expression for N A, in terms of all quantities. So that is why, this y A 2 is 0. So, after substituting this, all we have a numerical numbers of N A equals 2.925 10 to power minus 4 kilo mole per meter square second.

So, that is the first part or second part of the question, that calculate N A and N B; once we have N A, we can calculate N B as N A by 4 to make it 7.313 10 to power minus 4 5 kilo mole per meter square per second.

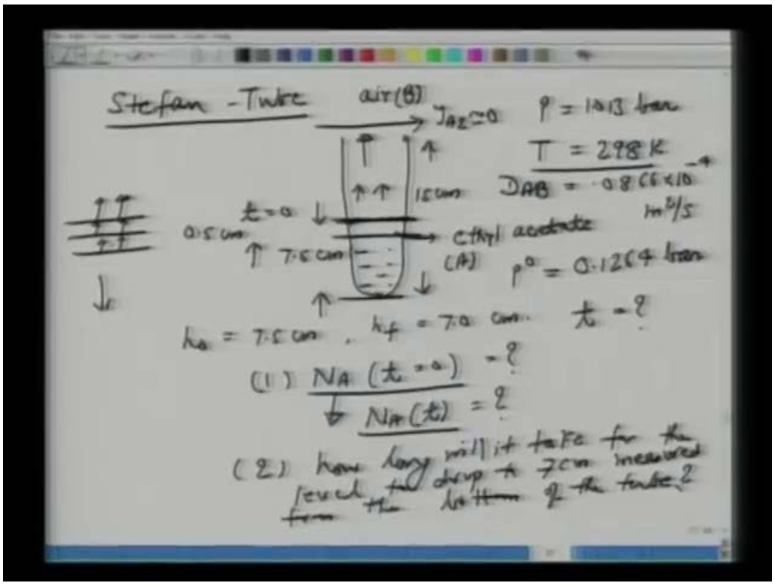
Now the question here was - what is the rate of formation of B? That was the question; at what rate B is formed? And what we have calculated - at what rate B diffuses between 1 and 2? So, at any location between 1 and 2 the diffusion flux is kilo moles per meter square per second, and now we are saying that since the reaction is very fast, steady state; whatever flux we have at any location between A and B, is the same as what we have at this surface, there is no lag there; and this all because of your assumption of a steady state and the reaction being very fast.

So, important that we understand the physical meaning of these two assumptions and see, how to be we obtain this rate of products. So, N B with what we obtain here is nothing but rate of production of B. So, they have same answers. One more example we will take here that is for a Stefan tube. So, that is being more complex, so we have 1, 2, 3 and this is about the Stefan's tube; if you recall a Stefan tube is a very simple tube, tubular arrangement, which is used to estimate or major the diffusion coefficients of B of A in B or B in A. So essentially, what we have, we have a tube filled with certain organics –

acetone, methyl acetate whatever we have, whose diffusion coefficients, we want to measure in B as it evaporates.

So, we have this schematic in we have the schematic in mind, that this organic vapour evaporates, it diffuses carried by this air on the top of it, and then it develops a concentration profile, with in this you have to make some measurements, how much amount of this organic is evaporated over a period of 8 hours, 10 hours, 24 hours and then we estimate this diffusion coefficients. So, we take this example of this Stefan tube very popular example here.

(Refer Slide Time: 21:48)



$P = 1.013$ bar

$T = 298$ K

$D_{AB} = 0.0866 \times 10^{-4}$ m^2/s

$p^o = 0.1264$ bar

$h_0 = 7.5$ cm, $h_f = 7.0$ cm. t - ?

(1) $N_A (t = 0)$ - ?

$N_A (t) = ?$

(2) how long will it take for the level to drop to 7 cm measured from the bottom of the tube?

So, we talking of this Stefan tube. So, what we have, a very simple u tube, it is filled with acetone. So, the problem reads that, this gets filled at till 7.5 centimeter. So, we have ethyl acetate filled in this tube, temperature, pressure is given P 1.013 bar, temperature is given as 298 Kelvin, D AB is given as 0.0866 10 to power minus 4 meter square per second, and total height of this tube is 15 centimeter.

So half of the tube is filled with ethyl acetate, and ethyl acetate evaporates, the rates of evaporation will of course, we decided by the temperature, and at this temperature, vapour pressure of ethyl acetate is given as 0.1264 bar. So ethyl acetate evaporates, and here we have a very gentle stream of air. So, again there are several restrictions here, idea of we look at carefully to ensure that whatever expression you have, we have developed one expressions, how to we use it and under what assumptions we are using it.

So, we do not have to violate any restrictions of a steady state alright; stagnant medium B B N B equal to 0 or we have equimolar counter molecule diffusions or we have non equimolar counter molecular diffusions N A and N B.

So, we have to look at those restrictions, and then we have to apply these equations. So, let us see that, where we apply those assumptions; we have been asked to as it evaporates it is swept by this air; the question is, how long will it take for the level to drop from at T equal to 0 from the 7.5 centimeter to drop to another 0.5 centimeter; in other words h 0 to start with a 7.5 centimeter, if you measure from the bottom, and we have final it drops to make it 7 centimeter.

So these are the two restrictions from here, that the question is how long will it take for this ethyl acetate level to drop from this level to this level; I drops, because ethyl acetate evaporates it comes to this air and air is swept. So, we can assume, if quantity of ethyl acetate is very small, which evaporates and very large amount of air that mole fraction of y A2; A is for ethyl acetate and B for air.

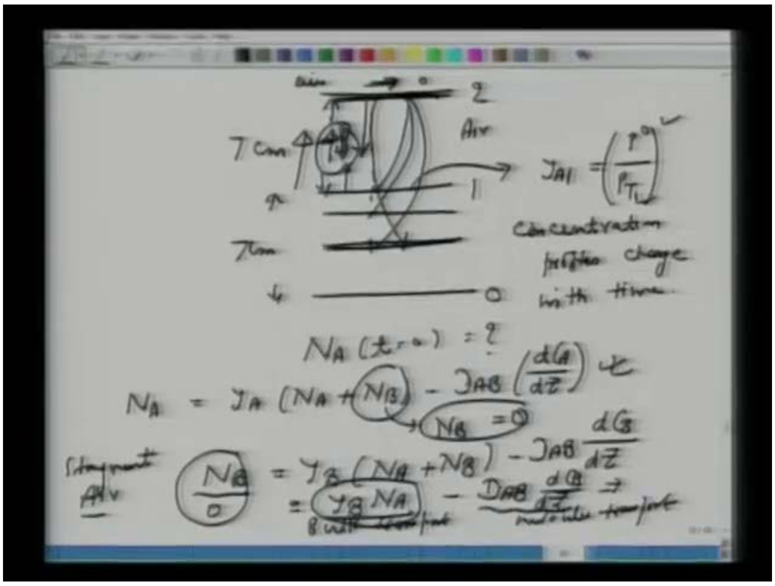
So, the mole fraction of ethyl acetate at the outlet of the tube is approximately 0. Question is of course, number one: first question is what is the molar diffusion flux at t equal to 0? So, at t equal to 0, when the level was 7.5 centimeter, half filled; what does the molar flux? So, when we have this questions; that means, molar flux it changes with time. So, if you recall the expression, which we developed, it is meant for a steady state; we assume that there is a steady state, and then we obtain the expression for diffusion flux; here the question is, at t equal to 0 what is a diffusion flux? That means, after sometime, this diffusion flux is going to change. So, it is dependent on time now right.

So, you have to assume, you have to very, very careful, how and when or if we can use that expression for diffusion flux of N A? So, that is the number 1 questions; question 2 as we said, how long will it take how long will it take for the level to drop to 7 centimeter measured from the bottom of the tube?

So, now let us revisit this tube; here the level decreases with time, so first we have the level here, now it decreases here, decreases here; and every time this evaporation of ethyl acetate, ethyl acetate.

So, it is quite important that we also understand, what would be the expected solutions? Before we solve numerically, we have a level of acetone, methyl acetate, which is 7 centimeter and on top of this, we have 7 centimeter of empty space are filled with ethyl acetate and the air; the 7 centimeter and 7 centimeter; then this level decreases; mole fraction of ethyl acetate at the exit of the tube is 0; and at the surface is determined the vapour pressure, not temperature is fixed, if the temperature is fixed, vapour pressure is fixed, atmospheric is fixed, concentration of ethyl acetate at the surface will also be fixed, but look at the gradient, concentration gradient - profile of the concentration gradient will keep on changing; why? Look at this profile here.

(Refer Slide Time: 28:17)



Before we solve, this is 2 here, and this is 1; this is 7 centimeter, and we have 7 centimeter of ethyl acetate to start, concentration here is 0, because we assume that as soon as it vapour of ethyl acetate comes here, it is swept by this flowing here; concentration here y A1 of ethyl acetate will be P 0 over the total pressure P T P A over P T.

One can calculate this, P 0 is fixed, total pressure is fixed; if these two are fixed, then we have some gradient like this, to start with and when the level drops is still 0, and this concentration level is still fixed here, where look at the profile, which has changed here; after sometimes the levels drops here, this is 0; this concentration is still fixed, we have another gradient.

So gradients - concentration gradient or concentration profiles profiles change with time, and the question was asked, that is why at N A at t equal to 0, what happens?

Now, let us apply start with the expressions, which we obtain to see how we can apply or to apply that equation, what are the restrictions? What are the assumptions we are making? So, the expressions for N A is N A equals y A N A plus N B minus T A B d CA over d z; first thing here, problem statement reads, that assume air is stagnant. So between 1 and 2, we are assuming that air is stagnant, which means we write N B equal to 0.

Now, when we say N B equal to 0, the more important here is to note that N B can also be written as y B N A plus N B minus D AB d C B of d Z; of course, if we make N B equal to 0, it is easier to integrate these equations and obtain what we obtain earlier, what we get earlier; but more important is, let us note down physically what does it mean, that N B equal to 0; air is a stagnant so this term is 0, but we have convective transport here - bulk transport which is y B N A minus, and then, we have the second term minus D AB d CB d by d z.

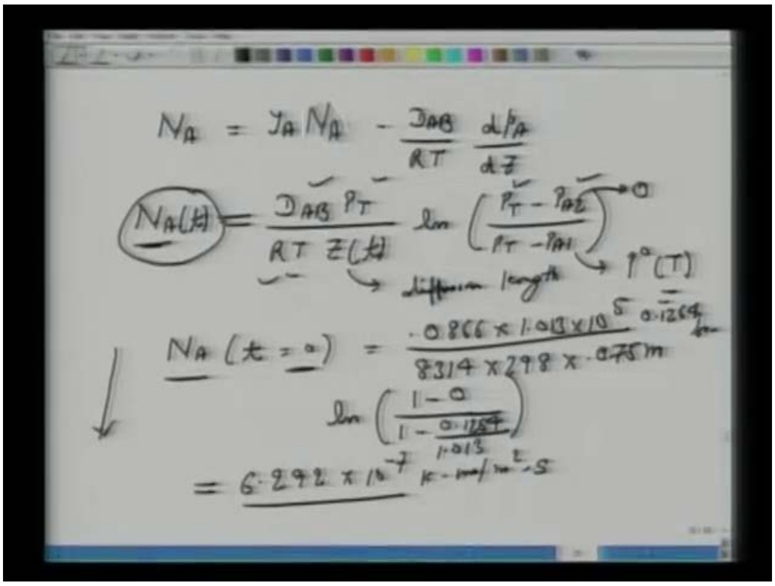
So, what it means? Air is still diffuses as ethyl acetate diffuses in this directions; air diffuses by molecular diffusion, but air is insoluble in ethyl acetate, which means, there is a induced bulk transport in this directions. So that, the transport of air by y B N A is same and equal to opposite to this molecular diffusion of B. So, although overall N B is 0 as seen by the stationary absorber the two components - one is a bulk transport and one is molecular transport for both A and B molecular transport given by this expression.

So, we do have a gradient of air, which goes like this, in this diffusion diffusion length between the top of a surface, top of this tube and the top of this ethyl acetate surface; but at any instance, whatever amount of air is diffuses by molecular diffusion, it is balanced by this bulk transport in the opposite directions.

So, this diffusion in this direction is balanced by this molecule, by this bulk transport, and we have a stagnant air in the medium. So, that is what the meaning of this air is a stagnant, a stationary observer sees air stagnant; no molecules of B diffuses or moves in one direction either from 1 to 2 or 2 to 1, but if the observer moves with the bulk velocity, he will see air diffusing in the directions opposite to the ethyl acetate right.

So, that is very important that we understand the physical meaning of each and every term, which we address in our first second or third lecture.

(Refer Slide Time: 33:24)



$$N_A = y_A N_A - \frac{D_{AB}}{RT}\frac{dp_A}{dz}$$

$$N_A(t) = \frac{D_{AB}\, P_T}{RT\, Z(t)} \ln\left(\frac{P_T - P_{A2}}{P_T - P_{A1}}\right)$$

$P_{A2} \to 0$

$P_{A1} \to P^{\circ}(T)$

$Z(t) \to$ diffusion length

$$N_A(t=0) = \frac{.0866 \times 1.013 \times 10^5}{8314 \times 298 \times .075\,m} \ln\left(\frac{1-0}{1-\frac{0.1264}{1.013}}\right)$$

0.1264 bar

$$= 6.292 \times 10^{-7}\ k\text{-}mol/m^2\text{-}s$$

Let us get back to this problem. So that is the meaning of N B is equal to 0; now, we put substitute here to obtain N A as y A N A N B is 0 minus D AB we can write C A in terms of partial pressure and D AB over R T as d partial pressure of A over this d z. one can integrate this equation, but already we have integrated our previous expression to obtain N A as D AB total pressure over R T Z l n P T minus P A 2 over P T minus P A 1 this Z is diffusion length; now look at this problem, we obtain this expression for a steady state; so that means, diffusion flux N A does not change with time, and here we see that expression, that NA depends upon Z, but Z is itself is a function of time, which means N A is also a function of time, because all the rest of the quantities they are fixed; P T P A2 we can assume 0, P A 1 partial pressure of A is nothing but the vapour pressure of ethyl acetate, temperature is fixed, all quantities are fixed. If Z changes with time, NA will also change with time. So, the question here was that what is the diffusion flux at their instance when the level is 7 centimeter?

So, we have essentially N A t equal to 0 equal to we all we have to do to substitute and put the correct value of z t equal 0. So, we have D AB as given as 0.0866 total pressure 1.013 10 to power to 5 divide by R 8314 298 into Z, which is 75 centimeter, this is 0.075

meter l n 1 minus 0 we divide by P T 1 minus vapour pressure is given 0.1264 divide by1.013. So, the vapour pressure of P, t is 0 is given, at that temperature is 0.1264 bar.

So, we have this, all we have to substitute and solve to obtain 6.292 10 to power minus 7 kilo mole per meter square second. So, the diffusion flux to start with t equal to 0 is so much, and as Z see, increases N A will decrease 1 over 7.So, that the first part of the questions the second part of the question is even more interesting.

So, the second part of the question was - how long will it take for a level to drop from Z1 to Z 2? And as we said earlier that if that level changes, diffusion flux is also changes with time, concentration profile also changes with time. So in reality, this is a unsteady state problem; out of any variables in a physical system, if one variable is changes with time, overall problem is unsteady state; but we are going to making use of, you know, well known quasi steady state or pseudo steady state approximations.

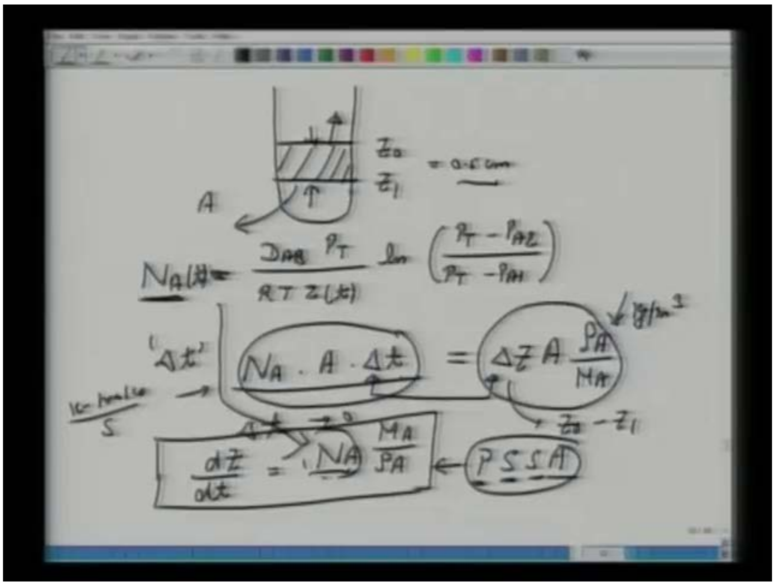
So, we also understand that - what is the physical meaning of this quasi steady state approximation? And how we are applying the expression which we obtain for a steady state? Now, here the level of A decreases very, very slowly; in fact, if you solve the problem, you will turn out to be that you will take 22 hours, 24 hours for the level of decrease of A decreases to some 0.5 centimeter by height.

So, if you has… So, the two rates: one is the rate of diffusion, and one is the rate of decrease in this level of the surface; just like, try to recall what we had earlier in the previous example, where a certain species diffuses, and then it reacts at the heterogeneous surface. So, there we have two rates: one is the rate of diffusion, and one is the rate of reactions.

So, whenever we have two rates, it is always the good idea to compare the two the rates of the two, you know two steps; it is possible that one rate is very fast, and another rate is very slow, in those cases one can make a quasi steady state, otherwise the problem make this if want to solve it mathematically, it is a very, very rigorous problems; you will have to set up the two governing equations: one equation for the diffusion, and one equation for the reaction rate, and in this case one other reaction, another rate is for the rate of decrease of this level, the two are couple together and they have to be solved simultaneously.

But if you make quasi steady state, which is as to be consistent with the physics; that the rate of decrease of this level is very, very slow; over that rate of over the time step, at which this level of ethyl acetate decreases, if we assume steady state; that means, we can still apply, what expression we had for diffusion flux. So, assuming this quasi steady state; that means, level decreases very, very slowly; one can a still apply the steady state expressions.

(Refer Slide Time: 39:01)



Now, if you go back to this, you know, we have, you know the same, just we call the tube here, and the level was this Z 0, it decreases to Z 1, and then, we said that already we obtain that expressions that N A is Z dependent D AB P T over R T z l n P T minus P A2 over P T minus P A1. So, when we obtain this relation, we said it is a steady state; now, we are saying that Z is also a function of time, and N t is also a function of time.

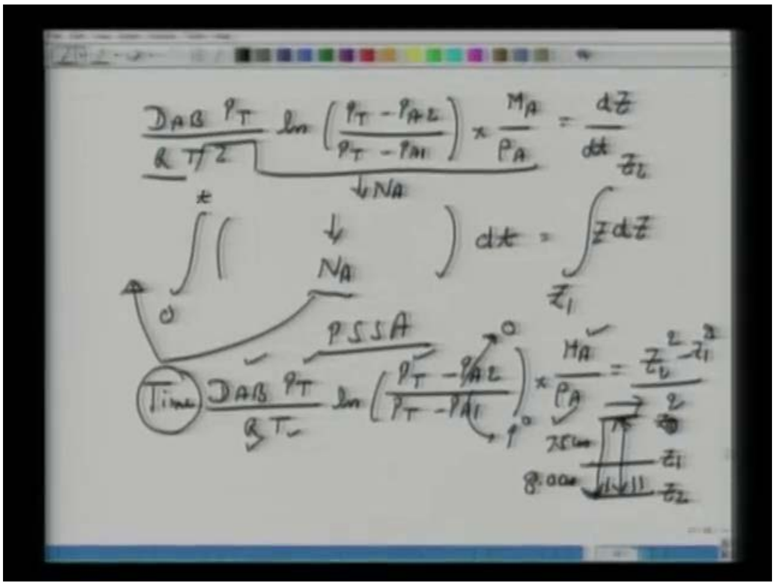
See, that is place, that is the step where we have to, you know very, very we have to be careful, in applying this quasi steady state, and here we apply this, because we said that this drop of 0.5 centimeter express over a longer time, and diffusion rate here is faster in terms of the rate of decrease of this.

So, now if you make a material balance of over the del t how much amount of A has evaporated and equate with this diffusion flux. So, we have N A moles per second per meter square of ethyl acetate, which evaporates over this cross sectional area of A. So, A is a cross sectional area over this del t. So, it is a material balance in one second so much kilo moles per moles of A diffuses over this del t.

Now, this is nothing but how much level has dropped in this del t time, which is del z into area this gives you differential volume multiplied by the density of ethyl acetate divided by this molecular weight to make it moles per second in total moles of A evaporated over del t equal to the quantity of ethyl acetate, which is lost between this Z 0 and Z 1; in limit of del t tends to 0 essentially, we have d Z over d t equals N A M A over rho A see expressions for d z by d t, at what level d z surface changes? We are writing it N A M A over rho Z, in reality N A is also a function of time, but we are assuming that N A is quite faster at the rate of this decrease of this level.

So, we again we are made use of P S S A Pseudo Steady State Approximations, Quasi Steady State Approximations. Now, all we do, you have two equations, which are almost pick up; we take this expression for N A and substitute here and we integrate.

(Refer Slide Time: 42:18)



So, if we now take that expressions and we integrate here, you will get D AB P T R T Z. So, this is the term of N A P T minus P A2 over P T minus P A1 into M A over rho A equals d Z by d t. Now we integrate, if you bring this term here. So, we have entire expressions like this, Z will come here, we have d t equals d z Z d Z going from Z 1 to Z 2 t equal to 0 to 2.

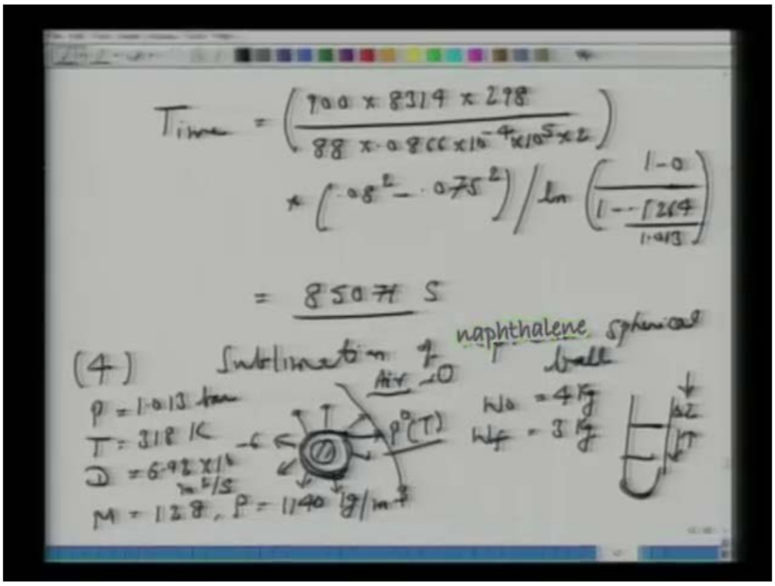
Now, again let us go back and see, where we are making these restrictions or assumptions of quasi steady state, entire rest of the terms is nothing but your diffusion flux N A, which we writing here. And when we integrate and we say that, if NA is a constant or does not change with time, then we can take it outside this integrate; and that is the place, we are making use of quasi steady state approximation, is very important that we understand instead of blinding memorizing some integrated expressions in applying.

Here is by making this quasi steady state approximations, pseudo steady state, the diffusion flux NA is constant over this time del t, because the level changes over a very, very long time; we can we can take out this N A as if it is a constant, D AB P T R T ln P T minus P A2 over P T minus P A1 into M A over rho A and we have T here (( )) and then we have Z 2 square minus Z 1 square over 2.

Now, all quantities are known here, total pressure, diffusion coefficients or this is your total time. So, this temperature here, let us write a time, this is a temperature, total pressure P A2 at the outlet of the tube is 0, because concentration is there is 0, P A1 is nothing but vapour pressure, which is given to us molecular weight, density of acetone, two heights: Z 2 square minus Z 1 square; if it is see the schematic, we have the top of the level, which was our Z 1 and we have Z 2 which is here, sorry we have this Z 0 and we have Z 1.

So to start with, this was 7.5 centimeter, and the question asks was, how long will it take to for the drop by 0.5 centimeter? This will become your 8 centimeter. So, this is the diffusion length, ethyl acetate evaporates from this surface and goes over this and swept by this air. So, all this quantities are known, you can calculate this time of diffusion.

(Refer slide Time: 45:42)



$$\text{Time} = \left(\frac{900 \times 8314 \times 298}{88 \times .0866 \times 10^{-4} \times 10^{5} \times 2}\right) \times \left(.08^2 - .075^2\right) \Big/ \ln\left(\frac{1-0}{1-\frac{.1264}{1.013}}\right)$$

$$= \underline{85071\ S}$$

(4) Sublimation of naphthalene spherical ball

Air ~0

$P = 1.013$ bar

$T = 318$ K

$D = 6.92 \times 10^{-6}$ m²/s

$M = 128$, $\rho = 1140$ kg/m³

$W_0 = 4$ kg

$W_f = 3$ kg

So, time of diffusion is t, all type substitutions 900 8314 298 900 will be the density of acetate molecular weight 88 diffusion coefficient 0.0866 10 to power minus 4 10 to power 5 into 2 into 0.08 square minus 0.075 square by 2, and this 2 is here divide by this ln 1 over 1 minus 0 1 minus 0.1264 divided by 1.013 total pressure into this, this will terms out to be approximate 85071 seconds. So, it takes a long time for this what level to ethyl ethyl is level of ethyl acetate to decrease from 7.5 centimeter to 8 centimeter?

Now, this is the third example we had, where we applied the same expressions for N A, in terms of bulk transport and the diffusion components, but here we are applying this quasi steady state very, very rigorously; we brought one more rate the rate at which the level of ethyl acetate decreases from one to another.

So at every step of decrease of the level, one has to assume that the other rate which is diffusion flux is stationary; in that case, we can make these assumptions and we can integrate the equations, and we can apply to find out total time for the level to decrease and what we do? If we take one more examples, which is very similar to what we had earlier, now it is a spherical coordinates; in our last lecture, we said that we can still apply the diffusion flux - the expression for diffusion flux in a spherical coordinates; however, we have to be careful that in case of a spherical coordinates, the cross sectional area or the area of this diffusion plane change it with the radius or with the distance.

So, it is moles per second, which is conserved, not moles per second per meter square, unlike in the Cartesian coordinates, when we say that there is a steady state, NA moles per second per meter square will are also be constant with time and along the Z directions. In case of a spherical coordinates, if you say it is a steady state, moles per second per meter square may do not change with time; but it will change with distance, because meter square changes with the distance 4 pi R 1 square then we have 4 pi R 2 square.

So, when we apply these equations, we have to be careful with the integrations; there has to be R distance dependents term, which has to be integrated; and a very common example, for such cases is evaporation of naphthalene ball. So, what we had earlier was evaporation of a ethyl acetate in tube, and then the diffusion length path is in Cartesian coordinate system.

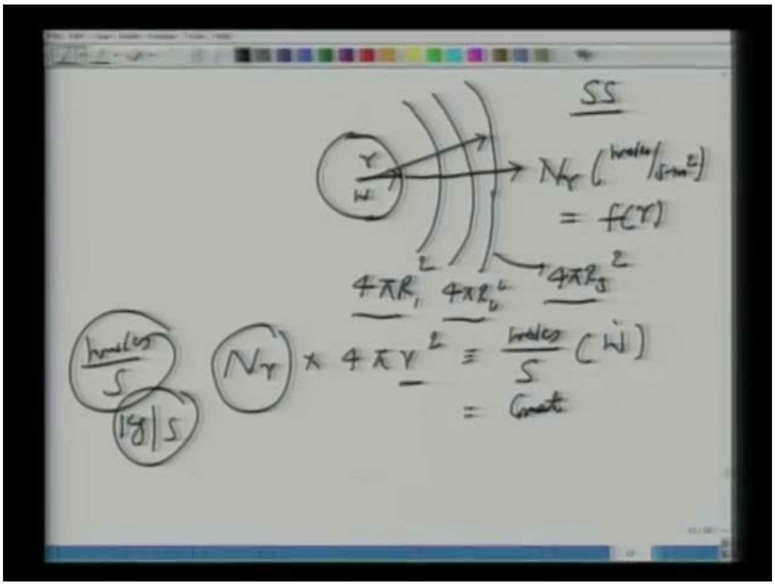
Now, we have a spherical naphthalene ball is diffuses, which evaporates in atmosphere, and then, the question ask is how long will it take for the radius of this naphthalene ball to decrease from say r 1 to r 2 or the amount of the naphthalene to decrease from w 1 to w 2. So the same principle, except now we are looking at this spherical coordinates.

So, let us go back to this example here, example 4, which is also very popular sublimation of naphthalene spherical ball. So, we have a naphthalene ball like this - spherical, it is given that to start with, it is weight is 4 kg, and as as it evaporates, it is strings and the final weight is 3 kg. So, the question is same, pressure is given P 1.013 bar, temperature is given 318 Kelvin, diffusion coefficient is 6.92 10 power minus 6 meter square per second, molecular weight of this naphthalene is given as 128, density is given as 1140 kg per cubic meter.

So, now look at the evaporation of this naphthalene. So, when it diffuses, when it first it has to evaporate. So, it evaporates into atmosphere, which is air. So, if we evaporate, then there has to be a concentration gradient. So, all it means here the concentration gradient or concentration at the surface is controlled by the vapour pressure or what we call sublimation pressure at the solute. So, the vapour pressure or sublimation pressure depended upon temperature. So, the concentration at the surface is controlled by this, and concentration in atmosphere will depend up on the composition of air; if you assume that as soon as this naphthalene comes out of this, it diffuses and it swept away by air; you can assume that the concentration at very far distance is approximately 0.

So, this problem is very similar, to what we had in earlier example, and we had this ethyl acetate the level decreases from here to here, and there is a diffusion length of del Z from here to here, here also we have a diffusion length from one set surface to the very (( )).

(Refer Slide Time: 52:05)

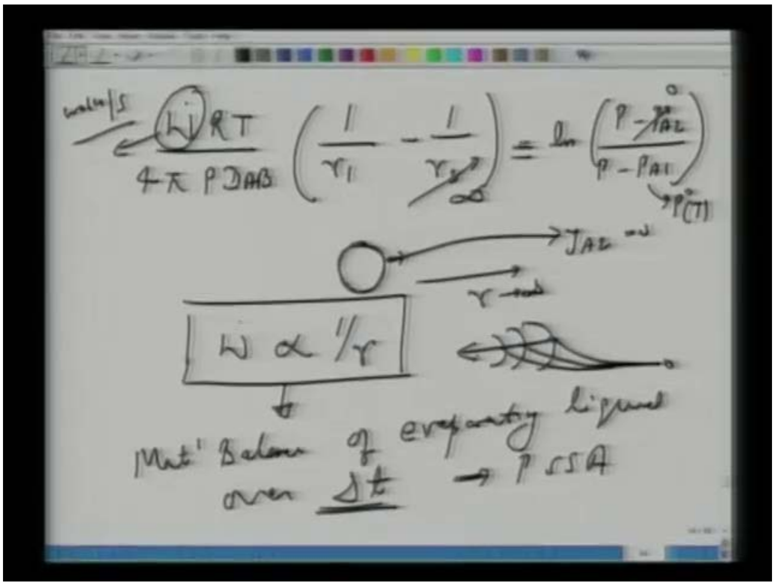


So let us get back to this problem, and redraw this - a schematic. So, at any instance, the radius is r, weight is w and naphthalene vapour diffuses into atmosphere. So, we have different, different planes of diffusion; which means the cross sectional area or the projector area or the area of this diffusion plane self changes from 4 pi R 1 square to 4 pi R 2 square to 4 pi R 3 square etcetera.

You can still go back and apply the same expressions, what we had done earlier here, what we obtain earlier, but more important is must we must realize that there is N r moles per second per meter square will be a function of r; although, it is a we are assuming steady state, because the very fact that the area itself changes.

However, N r 4 pi in multiplied by 4 pi r square, which will be moles per second of we call it W dot, this will be constant; all that the total moles per second moles per second or kg per second will be conserved, will be constant under steady state per kg per second per meter square or moles per second per meter square will not be constant with r. So, when we write down the expressions for N r and in the previous expressions and we integrate we have to ensure that we are making a correct integration.

(Refer Slide Time: 54:07)



So, we can always go back and integrate the previous expressions, which we had W dot R T over 4 pi D AB 1 over r 1 minus 1 over r 2 equals ln P minus P A 2 over P minus P A1. So, this expression we obtain for total moles per second of A diffusing in in a spherical coordinates; we can assume that size of this sphere is very small, and when it when the naphthalene evaporates, it goes into a very large, very long distance, which means we can assume r 2 in the limit, very large r 2 tends to infinity, P A2 is 0 at very far distance from here, r tends to infinity, concentration here is 0, P A 1 is decided by the vapour pressure or sublimation pressure at that temperatures; now we have a expressions for a steady state W 1 which is a function of r.

Now from here, we have to go back to our material balance over material balance of evaporating liquid over del t and when we write such expressions, again we have to make use of quasi steady state approximations, because every time the size of this sphere changes with time, which means the concentration gradient from the surface to this very far, which is 0 will also change with time. So in reality, it is a unsteady state problem, what we are trying to make use of quasi steady state assumptions.