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Lecture - 13 Mass transfer theories

Welcome to 5th lecture of module-2 on Mass Transfer Operation. In this lecture, we will discuss the Mass Transfer Coefficient, and then the theories of mass transfer in turbulent conditions. Before going to the next lecture, let us have small recap on our previous lecture.

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Recap , BL Theory in Man Transfer , Film theory

In our previous lecture, we have considered boundary layer theory in mass transfer. And then the second case, we have considered film theory. So, in film theory mainly we have discussed that the there is a stagnant film near the gas liquid interface. And then the concentration profile through the stagnant film is linear as with respect to the film theory or as described by the film theory.

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Here we will discuss other mass transfer theories in the turbulent flow condition, one such theory is penetration theory. As you can see there are two different no figures over here. One is the bubble gas bubbles, and there is a liquid particles which are moving along the surface. And then the other case in case of b as it is shown, it is there is a pool of liquid. And there is a liquid particles, which goes to the and above the pool of the liquid you have a gas layer. And then the liquid particles goes to the surface for a certain period of time, it stays with the contact with the glass film, and then it return back to the bulk.

So, penetration theory was explained by Higbie's in 1935. And it is observed in many situation that the time of exposure of the fluid to mass transfer is very short. So, exposure of fluid to mass transfer for a period of time which is very short, in most many situations in case of the mass transfer. So, if the time of exposure is very short, what happens? The concentration gradient which is discussed in the film theory, and which is a characteristics of the steady state conditions would not have time to develop. So, for short contact time, the concentration gradient will not attain or will not develop. So, it is Higbie explained as a bubble of gas rises through a liquid which absorbs the gas.

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And in the now in this case a particle of liquid b you can see over here, a particle of liquid b, initially at the top of the bubble, and it was in contact with a with the gas for a period of time theta, it requires for the bubble to rise a distance equal to its diameter that means, while the liquid particles will slip from top to the bottom or to the along the surface it slips, and comes to the bottom and it is discharged over here.

An extension of the cases where the liquid may be in turbulent motion as shown in figure b, an eddy of b which is rising from the turbulent depth of the liquid and remaining exposed for a time of theta to the action of the gas. So that means this no tiny liquid droplet will go to the gas liquid interface remain exposed with the gas for a period of time, which is defined here as theta for the mass transport to take place.

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In this theory, the time of exposure which is considered theta is taken as constant for all eddies or for all liquid particles. Initially, the concentration of the dissolved gas in the eddy is uniformly C A0. So, at initial conditions the concentration of the dissolved gas is considered as C A naught, and it is the same over here as well in this case as well. And internally the eddy is considered to be stagnant.

When the eddy is exposed to the gas at that surface, the concentration in the liquid at the gas-liquid surface is C Ai. So, once it will come over here, the concentration of component a in this in the liquid at the gas liquid interface is C Ai, which may be taken as equilibrium solubility of the gas in the liquid. So, this can be calculated from the solubility of component A at a particular pressure which is dissolved in the liquid.

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Now, it is assume that equilibrium is immediately attained by the surface layer that means, as soon as the liquid element comes in contact with the gas phase the solute which will transfer from the gas to the liquid, it will immediately attain equilibrium at the surface layer. And that is why a process of unsteady state molecular diffusion occurs, and that the element is remixed after a fixed interval of time, so that means the element again come back to the bulk, and again return to the surface.

So, in this calculation the depth of the liquid element is assumed to be infinite. So, why whether this assumption is correct? It will be justified when the time of exposure is sufficiently short for the penetration that means, the gas penetrate is a very small amount, because the length of exposure of that element at the surface is very short. Due to this short surface, the distance in the bulk is much higher and which can be considered as infinite.

Throughout, the existence of velocity gradient within the fluid is ignored. So, in this case the velocity gradient within the fluid is neglected and the fluid at all depths is assumed to be moving at the same rate as the interface. So, it is no rate, so there will not be gradient of the velocity of all the liquid element with respect to the free surface that is at gas liquid interface.

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Now, let us take a problem like diffusion of A away from the interface in the z-direction the Fick's second law we can reduce to del C A del t would be equal to D del 2 C A del z 2 that is without chemical reaction. Now, the following boundary conditions will apply at t is equal to 0, and z greater than 0, and less than infinity, C A would be C A naught. At t greater than 0, at the gas-liquid interface at z is equal to 0, C A would be C A i. T greater than 0, at any time z equal to infinity that is in the bulk is C A would be C A naught. So, C A naught is considered as the concentration in the bulk phase, and C A i is the equilibrium value at the interface.

Now, we need to solve this problem to find out the concentration profile and the flux at the interface. Now, it will be very convenient, if you work in terms of the deviation variables that means, C dash would be C A minus C A naught that is the concentration in the bulk which is constant. And this C A is the any concentration, so C dash is C A minus C A naught. We can write equation-1 as del C dash del t would be equal to D del del square C dash by del z square, this is equation-2.

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Now, since C A naught is constant with respect to time and z, so it is constant. The boundary conditions we can write in terms of the deviation variables that is t would be at t equal to 0 z greater than 0, and less than infinity. C dash would be 0, because it is C A minus C A naught. So, at this t would be equal to 0, C A would be C A naught minus C A naught so, then C dash would be equal to 0.

At any time t greater than 0, z equal to 0 that is at the interface, it will be the interfacial concentration C A i. So, C dash would be at the interface that is C dash i would be equal to C A i C A would C A i minus C A naught. And at t greater than 0, z equal to infinity that is at the bulk, it will be similar to this, because at bulk its C A naught. So, it is C dash would be 0. So, this is the boundary conditions, which are defined with respect to the deviation variables or in terms of the deviation variables.

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The boundary conditions are necessary and sufficient for equation-2; this is the equation-2 which is first order with respect to time, and second order with respect to z. The equation we can most conveniently solve by the method of Laplace transform, and used for the solution of unsteady state thermal conduction problems. So, we can easily solve this problem using the Laplace transform method.

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Problem 1: solution
Diffusion of A away from the interface (z – direction) the Fick's second law reduces to $\frac{\partial C_{x}}{\partial t} = D \frac{\partial^{2} C_{x}}{\partial z^{2}}$ (1) The following boundary condition apply $t = 0$ $0 < z < \infty$ $C_{x} = C_{x}$, $t > 0$ $z = 0$ $C_{x} = C_{x}$, $t > 0$ $z = \infty$ $C_{x} = C_{x}$, $C_{x} = concentration in the bulk of the phase C_{x} = the equilibrium value at the interface.$
Solve the above problem to find out concentration profile and flux at the interface. Solution: By definition, the Laplace transform \overline{C} of C' is given by:
$\overline{C}' = \int_0^\infty e^{-pt} C' dt$

By definition, the Laplace transform C dash bar of C dash is given by so if we considered C dash is our variable, its Laplace transform will be C dash bar and which we

can write by definition C dash bar would be equal to integral 0 to infinity e to the power minus p t C dash dt, this is equation-3.

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Problem 1: solution	
Diffusion of A away from the interface (z – direction) the Fick's second law reduces to $\partial C_A = D \frac{\partial^2 C_A}{\partial z^2}$ (1) The following boundary condition apply $t = 0$ $0 < z < \infty$ $C_A = C_{A_0}$ $t > 0$ $z = 0$ $C_A = C_{A_0}$ $C_{A_0} = C_{A_0} = C_{A_0}$ $C_{A_0} = C_{A_0} = C_{A_0}$	
$c_{A} = uc$ equinorium value at the interface. Solve the above problem to find out concentration profile and flux at the interface.	
Then $\frac{\overline{\partial C'}}{\partial t} = \int_0^\infty e^{-pt} \frac{\partial C'}{\partial t} dt$	
$\frac{\overline{\partial C}}{\partial t} = \left[e^{-pt} C' \right]_0^\infty + p \int_0^\infty e^{-pt} C' dt$ $= p \overline{C'}$	

Now, in our case it is equation-1 is del C A del t would be equal to D del 2 C A del z 2. So, we have to take Laplace transform of the left hand side that is del C A del t, and also on the right hand side that is D del 2 C A del z. So, taking the Laplace transform of the left hand side from this equation so, we can write del C dash bar del t would be equal to integral 0 to infinity e to the power minus pt del C dash del t d t.

So, if you just integrate it, it would be e to the power minus pt C dash limit 0 to infinity plus p integral 0 to infinity e to the power minus pt C dash dt. Now, from this if you just put the limit, and this part is nothing but is C dash bar which is the Laplace transform of C. And so this can be written as p into C dash bar.

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Now, since the Laplace operator is independent of z. The right hand side, we can write del 2 C dash bar del z 2 would be equal to del 2 C dash bar del z 2. So, here so z it is you know Laplace operator is independent of z. So, we can write this. Now, thus taking the Laplace transform of both side of this equation, we can write the left hand side which we have derived earlier using the Laplace is p C dash bar would be equal to D del 2 C dash bar del z 2 ok. And if you just rearrange this equation, so you will get del 2 C dash bar del z 2 minus p by D C dash bar equal to 0. So, this is equation-7.

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Problem 1: solution
Diffusion of A away from the interface (z – direction) the Fick's second law reduces to $\frac{\partial C_{s}}{\partial t} = D \frac{\partial^2 C_{s}}{\partial t}$ (1)
The following boundary condition apply $t = 0$ $0 < z < \infty$ $C_{A} = C_{A_{0}}$ ∂t ∂t ∂z^{2}
$t > 0$ $z = 0$ $C_A = C_{A_0}$
$t > 0$ $z = \infty$ $C_A = C_{A_0}$
$C_{A_0} = $ concentration in the bulk of the phase
$C_{\mathcal{A}_i}$ = the equilibrium value at the interface
Solve the above problem to find out concentration profile and flux at the interface.
Solution: Equation (7) is an ordinary second order linear differential equation in \overline{c}
The solution of equation (7) is $\partial^2 \overline{C}$, $p \equiv 1$, \overline{C} = $B_1 e^{\sqrt{(p/D)} z} + B_2 e^{-\sqrt{(p/D)} z}$.
$\frac{\partial z}{\partial z^2} - \frac{r}{D}C = 0$

This equation-7 is an ordinary second order linear differential equation in C dash bar. And the solution of this equation, we can write as C dash bar would be equal to B 1 e to the power root over p by D z plus B to e to the power minus root over p by D z.

Problem 1: solution
Diffusion of A away from the interface (z – direction) the Fick's second law reduces to $\frac{\partial C_{x}}{\partial t} = D \frac{\partial^{2} C_{x}}{\partial z^{2}}$ (1) The following boundary condition apply $t = 0$ $0 < z < \infty$ $C_{x} = C_{x}$ $t > 0$ $z = 0$ $C_{x} = C_{x}$
$t > 0$ $z = \infty$ $C_A = C_{A_0}$ $C_{A_0} = \text{concentration in the bulk of the phase}$ $C_{A_0} = \text{the equilibrium value at the interface}$ Solve the above problem to find out concentration profile and flux at the interface.
Solution: when: $z = 0$, $C_A = C_A$, and $C' = C_{A_i} - C_{A_b} = C'_i$ & when: $z = \infty$, $C_A = C_{A_b}$, and $C' = 0$ Hence: $B_1 = 0$ And: $\overline{C'} = B_2 e^{-\sqrt{(p/D)} z} = \overline{C'_i} e^{-\sqrt{(p/D)} z}$

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Now, as we know when z is equal to 0, C A would be C A i, and C dash would be equal to C A i minus C A naught would be C i dash. And when z is equal to infinity, C A would be equal to C A naught, and C dash would be 0. So, if we use this boundary conditions in our earlier equation-8, we can calculate B 1 would be 0. So, then our equation will reduce to C dash bar would be equal to B 2 e to the power minus root over p by D into z, so which is equal to C i dash bar e to the power minus root over p by D z. So, this is equation-9.

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Now, we need to find out this B 2 or C i dash bar. So, B 2 is equal to integral 0 to infinity C A i minus C A naught e to the power minus pt d t. So, if you just integrate it, it will be 1 by p C A i minus C A naught.

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So, if we substitute this in the earlier equation, we will get C dash bar would be equal to 1 by p C A i minus C A naught e to the power minus root over p by D z. Now, this is the Laplace transform of C dash that is the deviation variables. Now, if we take the inverse Laplace of this, we will get C dash which is equal to in terms of the deviation variables C A minus C A naught would be equal to C A i minus C A naught complementary error function Z by 2 into root over D t.

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So, if you just rearrange the equations from here, we can just rearrange like this C A minus C A not divided by C A i minus C A naught. So, taking this term over here, and then we will have in the right hand side complimentary error function z by 2 root over D t, so which is written over here. Now, this complementary error function of z by 2 root over D t can be written as 1 minus error function of z by 2 root over D t, so this is equation-12. Here erf X is error function of X, and erfc X is the complementary error function of X. So, error function already we have discussed in our earlier discussion.

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So, by definition complementary error function is equal to 2 by root pi integral X to infinity e to the power minus x square d x. Since, 0 to infinity e to the power minus x squared d x is equal to root pi by 2. The error complementary error function goes to 1 to 0 as X goes to 0 to infinity. So, when x goes to 0 to infinity, then the complementary error function will vary from 1 to 0.

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The concentration gradient is then obtained by differentiation of the equation-12, which is this is the equation-12. And if you just take the differentiation of this equation with

respect to z, we will get the concentration profile. So, taking the no derivative of these, it will be 1 by C A i minus C A naught del C A del z would be equal to del del z of 2 by root pi integral z by 2 root over D t to infinity e to the power minus z square by 4 D t into d of z by 2 root over D t.

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So, this will be del C A del z would be equal to minus C A i minus C A naught 2 by root pi into 1 by 2 root over D t into e to the power minus z square by 4 D t. And then if we just rearrange, it will be minus C A i minus C A naught 1 by root over pi D t e to the power minus z square by 4 D t. So, this is equation-13.

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The mass transfer at any position z at time t is given by N A t that is the flux, at any time t which is equal to minus D del C A del z. So, if you substitute del C A del z from this equation in the flux equation, we will get C A i minus C A naught into root over D by pi t e to the power minus z square by 4 D t. So, this is equation-14.

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Problem 1: solution	
Diffusion of A away from the interface (z – direction) the Fick's second law reduces to $\frac{\partial C_d}{\partial t} = D \frac{\partial^2 C_d}{\partial z^2}$ (1) The following boundary condition apply $t = 0$ $0 < z < \infty$ $C_a = C_a$, $t > 0$ $z = 0$ $C_a = C_a$, $t > 0$ $z = \infty$ $C_a = C_a$, $C_a = \text{concentration in the bulk of the phase}$ $C_a = \text{the equilibrium value at the interface}$ Solve the above problem to find out concentration profile and flux at the interface.	
Solution: The mass transfer rate per unit area of surface is then	
$(N_{A})_{t,z=0} = -D\left(\frac{\partial C_{A}}{\partial z}\right)_{z=0}$ $= (C_{A_{t}} - C_{A_{0}})\sqrt{\frac{D}{\pi t}}$ The point value of mass transfer coefficient is therefore $\sqrt{D/\pi t}$	

When at z is equal to 0 that is at the interface at any time t the flux, we can define is equal to minus D del C A del z at z is equal to 0 that is mass transfer rate per unit surface at the gas liquid interface. So, if we use no this z is equal to 0 in our earlier equations

over here, so this will be 1. So, N A t at z is equal to 0 would be C A i minus C A naught root over D by pi t, so which is written over here. So, this is equation-15.

And the point value of mass transfer coefficient K L will be root over D by pi t. So, this is no very well-known output from the penetration theory, where mass transfer coefficient is related with the square root of diffusivity by pi theta. So, it is a square root dependence of diffusivity in case of penetration theory. And we have seen in case of film theory, the diffusion coefficient is directly proportional to d a b that is K L would be equal to d a d a b by delta.

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Now, let us take an example in a gas-liquid contactor, a pure gas is absorbed in a solvent and the penetration theory provides a reasonable model by which to describe the transfer mechanism. A fresh solvent is exposed to the gas; the transfer rate is initially limited by rate at which the gas molecules can reach the surface.

If at 293 Kelvin and a pressure of 1 bar the maximum possible rate of transfer of gas is 50 meter cube per meter square second, so this is the rate of transfer of gas, express this as an equivalent resistance, when the gas solubility is point 0.04 kilo mole per meter cube. The second problem is if the diffusivity in the liquid phase is given 1.8 into 10 to the power minus 9 meter square per second, at what time after the initial exposure will the resistance attributable to access of the gas be equal to about 10 percent of the total resistance to transfer.

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So, let us consider bulk concentration, which is equal to 1 by 22.4 that is volume into 273 by 293, which is 0.0416 kilo mole per meter cube. So, we can calculate the bulk concentration. Initial mass transfer rate which is given is 50 meter cube per meter square second. And if you just multiply with the bulk concentration, it will give the no initial mass transfer rate in terms of kilo mole per meter square second, it is 2.08 kilo mole per meter square second.

Now, the concentration driving force in the liquid phase is 0.4 minus 0 that is it is a no pure gas. Initially, there is no solute in the liquid, because it is fresh solvent which is exposed to the gas. So, since it is fresh solvent, there is the solute concentration is 0. So, we can calculate the concentration driving force, which is 0.04 kilo mole per meter cube. The effective mass transfer coefficient initially is 2.08 divided by 0.04, so this is 52.0 meter per second. So, this is the initial effective mass transfer coefficient initially.

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Now, equivalent resistance is 1 by mass transfer coefficient which is 0.0192 second per meter. So, equivalent resistance we can we have calculated. Now, when this constitutes 10 percent of the total resistance, it is given over here. This constitutes equals to about 10 percent of the total resistance. So, the liquid phase resistance will be 90 percent that is 0.0192 into 9. So, the liquid phase resistance would be 0.1728 second per meter. The liquid phase coefficient will be 5.78 meters per second, so if you can calculate from here from this resistance.

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Now, regular surface renewal, it is important to note that the mass transfer rate falls off progressively during the period of exposure, theoretically from infinity at t is equal to 0 to zero at t is equal to infinity, so that is the theoretical mass transfer rate, which will fall from infinity to 0 at time t to infinity.

Now, assuming that all the surface elements are exposed for the same time that is t e that is Higbie's assumption, from equation 15, the moles of A n A transferred at an area A in time t e is given by this. This is the moles transferred no with the area and time of exposure A and t e, it will be C A i minus C A naught root over D by pi area into area integral 0 to t e dt by root over t. So, now if you just integrate it, it would be 2 into C A i minus C A naught A root over D t e by pi.

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Now, from here the average rate of mass transfer per unit area over the exposure time t e is given by, so we will get the average rate of mass transfer or the flux N A would be equal to 2 into C A i minus C A naught root over D by pi t e, so that is the average rate over the interval t is equal to 0 to t is equal to t e, which is twice the point value at t is equal to t e.

So, at point value it is basically we have seen N A would be equal to C A i minus C A naught root over D by pi t e and so in this case, it is the twice the average rate of mass transfer. So, from this we can write the mass transfer coefficient K L would be 2 into root over D by pi t e. Thus, the shorter the time of exposure the greater is the rate of mass

transfer. As the time will be shorter, the mass transfer rate will enhance from this equation.

Now, no precise value can be assigned to t e, in any industrial equipments although its value will clearly will become less as the degree of agitation of the fluid is increased. So, as the turbulence in the fluid will increase, its value will essentially decrease the time of exposure will essentially decrease. So, there is no particular value which can be assigned to any industrial equipment.

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Now, let us take another example a deep pool of ethanol is suddenly exposed to an atmosphere of pure carbon dioxide and unsteady state mass transfer governed by Fick's law, which takes place at a time of 100 second. What proportion of the absorbed carbon dioxide will have accumulated in 1 millimeter layer closest to the surface in this period. Given that D C O 2 in ethanol is 4 into 10 to the power minus 9 meter square per second. So, diffusivity is given.

Now, the accumulation in the 1 millimeter layer near the surface which will be equal to the amount of carbon dioxide entering in the layer from the surface less that leaving in the course of 100 seconds. So, this will be the difference between the two, which is entering and which is leaving, so that will govern the accumulation in that layer.

Now, the mass transfer rate at any position y and time t is given by equation-14, which we have seen. N A t would be equal to C A i root over D by pi t e to the power minus y square by 4 D t. N A t we know from the Fick's law, it is minus D del C A del z, and which is equal to if you just substitute, it will be C A i minus C A naught root over D by pi t e to the power minus z square by 4 D t. Here N A is expressed in mole per unit area and per unit time and C A naught is zero, because the solvent is pure ethanol.

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So, considering unit surface area, the mole transfer in time t e at depth y which can be written as C A i root over D by pi integral 0 to t e t to the power minus half e to the power minus y square by 4 D t into d t. Now, putting y square by 4 D t is equal to X square, we can get t to the power minus half would be equal to 2 into root over D x by y. And d t would be equal to y square by 4 D into minus 2 by X cube d X.

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So, the integral would be integral infinity to X e y square by 4 D into minus 2 by X cube into 2 into root over D into X by y e to the power minus X square d X. And then we can write it will be minus y by root over D integral infinity to X e X to the power minus 2 e to the power minus X square d X.

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So, the molar transfer per unit area we can calculate, it would be C A i root over D by pi into minus y by root over D into e to the power minus X square into minus X to the power 1 with a limit infinity to X e minus integral 0 to X e minus 2 X e to the power

minus X square into minus X to the power minus 1 d X. So, this is the molar transfer rate per unit area.

Now, if you just simplify C A i into minus y by root pi whole into minus X e to the power minus 1 e to the power minus X e square plus 2 into integral X e to infinity e to the power minus X square d X. So, it will be we can write this will be equal to C A i into y by root pi whole into 2 into root over D t e by y e to the power minus y square by 4 D t e minus root over pi complementary error function y by 2 into root over D t. So, this is we can simplify as like this.

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Now, the values which are given D is equal to 4 into 10 to the power minus 9 meter square per second and t is 100. Now, if you put this value at y is equal to 0, the mole transfer we can calculate. So, from the earlier equation. So, this is the moles transfer at y is equal to 0, 7.14 into 10 to the power minus four C A i. So, this mole transfer in terms of the interfacial concentration.

Similarly, at y is equal to 10 to the power minus 3 meter, the mole transfer can be calculated using this no equation. And these are tabulated function complementary error function values can be taken from the table. And it will be finally, give the values of no mole transfer at y is equal to 10 to the power minus 3 meter is 1.19 into 10 to the power minus 4 C A i.

So, now if we take the portion of the material retained in the layer, it will be 7.14 into 10 to the power minus 4 C A i minus 1.19 into 10 to the power minus 4 C A i divided by 7.14 into 10 to the power minus 4 C A i which is 0.83 that means 83 percent of the material which will be retained in the layer. So, thank you for your attention, and attending this lecture. And we will continue the mass transfer coefficient in turbulent flow in the next lecture.