

Environmental Quality: Monitoring and Analysis
Prof. Ravi Krishna
Department of Chemical Engineering
Indian Institute of Technology – Madras

Lecture – 47

Interphase Mass Transfer – Boundary Layer and Mass Transfer Coefficient

(Refer Slide Time: 00:28)

Inter-phase Mass Transfer

$\eta_A(\text{flux}) = \frac{\text{Driving force}}{\text{Resistance}} \rightarrow (\quad)$

Convective Resistance $\propto f(v)$ structure of fluid

Laminar flow \rightarrow fluid is arranged orderly

Turbulent flow \rightarrow eddies are present

So, we will continue from yesterday we were discussing, again the continuation of mass transfer fundamentals. So, what we were discussing yesterday is this issue of say flux is defined as a driving force over resistance. So, this driving force as we had discussed earlier is the difference in chemical potential or an equivalent difference in something. So, it is usually a difference in concentration, we will come to that what it means. In other words, this driving force is the difference from equilibrium to the departure from equilibrium, how far it is from equilibrium.

So, one of these 2 terms has to be an equilibrium related term, we will get to that, and the resistance is related to the actual transport of this molecule, how quickly or how well efficiently it can move from one place to another place. So, the resistance depends upon the nature of the molecule and nature of the fluid and the interaction with them and all that okay. So, we were also discussing yesterday the flux equals this general j_{Ai} , we apply this to every scenario.

Then when we look at interface mass transfer, when you look at interface, the interface between two phases, so at the surface, the interface we are looking at, material has to go in this direction. So, this is the fluid that is moving in this direction, the velocity is in this direction, but interface mass transfer occurs in this direction, okay. So let us say it is going from water to air, this is one, yesterday's class we looked at, solid to air, sediment to water and that kind of thing.

So, sediment water is a simpler system for other reasons, but it is the same, at the interface it is very similar. So, look at water to air. So right here, there is a velocity of the water. Let us assume that the water is not moving for the time being, it is just a semi rigid surface and here, so we have looked at the structure, we have also established that when there is some bulk motion because of convection, this term becomes more prominent, it starts becoming prominent. When there is no motion at all, then this term becomes dominant.

When there is a little bit of motion, this term starts increasing in magnitude, at some point this will become more than the diffusion okay because this will dominate okay. So because we are saying that is true, the next relationship is what happens to the convection, the extent of convection at a surface depends on the velocity okay. So, this term here, the convective term here or bulk or advective or bulk flow, see these are all just to indicate that it is not diffusion, could be any of these things.

It could be in whatever manner it is moving, but the fluid itself is moving here that is the idea. This is the function of now the velocity at that particular location okay and also the structure. So we also stopped at a point where yesterday we said that very close to the surface at very low velocities, you will find that the fluid moves in nice, in an almost layer like arrangement. The velocity of each one, velocity is increasing, this velocity is higher than this, this velocity is higher than this. So, motion is happening like this, this is at low velocity.

Theoretically, what we are saying is that at the surface velocity is 0. Sometimes, it is a theoretical assumption, it is easy for the mathematical problem, but otherwise it need not be 0 and it is very difficult to measure at the surface and we will come to that in a minute. So, the point behind this is because the overall mass transfer rate depends on these two terms, let us forget diffusion is always happening, do not worry about that, that is there, but the other term here changes as a function of velocity.

Because what happens is that as we increase velocity, this starts becoming more and more chaotic and there is more turbulence and this turbulence it moves like this, and if you have very high velocity, scale of this convection increases and it keeps on going at the surface itself and you can imagine that. So if you take a liquid pour it very slowly on a surface as against give it a lot of force, you can see that the fluid is not just gently flowing on the surface, it is getting turbid. So, these are called as eddies.

So, the scale of the eddies depend on the velocity itself and also on the geometry. So, it is a very smooth surface, you will get one kind of eddies. If the surface is rough or it has blocking unit or something like that, then it may cause more circulation, and there is a lot of energy loss and all kinds of things can happen. So, our interest is in if the mass transfer has to happen in this direction, is there anything else that is helping the chemical to move from this point to this point and this convection helps.

The convection is a function of velocity scale and all that. So, when it is a straight line, when the flow occurs in straight line, we call it as laminar, the fluid arranges itself is arranged more or less, see this is not very accurate. When we say straight line, it is not a straight line, you will see if you go and look at it with a microscope, for example even if I draw a straight line with a pencil if you go and take a microscope, you will see some small this things, so it is straight line at some scale and the scale of eddies or scale of non-uniformity is very small there okay.

But by and large, it is relative to us, so compared to this what we call as turbulent flow where the eddies are present are larger, along with that the eddies are larger and there is also fluctuation in all three directions of the flow okay and diffusion is already happening. Diffusion is always happening within a region, it is continuously happening. So, if there is a concentration gradient, diffusion will happen, along with it, this is also happening. Any of you not clear about this particular equation, any questions on this?

“Professor – student conversation starts.” If the system is well mixed, is it required that diffusion is still there? Diffusion will, can take place, diffusion always taking place, but then diffusion is irrelevant, this velocity is so huge that, diffusion will always be there. **“Professor – student conversation ends.”** Let me give you an example. So, if you have a conveyor belt

as the ones you have seen airports, let us say that they have a gradient. Normally what you see is a straight conveyor you know, these walkways that you have in airports, we do not have to move, it just moves.

You stand on it, it will move right, but let us say if there is a small gradient, small angle to this, say the theta angle and this is conveyor belt is moving in this direction. So, which means that is equivalent to bulk flow. If I keep an object here and the object will move at the speed of the belt, but let us say I keep an object which is like a ball, along with your belt flow, the ball is also rolling. The ball is rolling because of potential difference, it has its own potential, it wants to go down, it will roll.

So, the ball is rolling and if I move the conveyor belt very fast, the ball will also continue rolling, but the belt is moving fast and its speed at which it reaches this point is combination of both. So, no matter what you are doing, gravity is still acting. Let us say some guy comes and takes his ball and throws it, still gravity is acting, yeah. So gravity is always there, the potential difference is always there. The question is from an engineering point of view when we are estimating the rate and all that, do we need to really bother about that or is it mathematically it becomes more complex if you do diffusion and advection together.

It is one more term to solve, so we neglect that if the terms are big. So, this is order of magnitude of these things are important in this case. So, we do these kinds of considerations for okay. So the idea is this, so if just laminar flow, diffusion is occurring and at the interface there is a small convection which is carrying it to the next level and it goes again here and so the material is traveling in this direction roughly where it is also being carried in the x direction, but it also going up. You are following.

The fluid is in this direction predominantly, so a mass that is here it is taking this trajectory roughly, it is getting into it. So, effectively in this given region, there is a net mass transfer in this direction, but it is not occurring, fluid is not static, so it cannot move directly upward, it is getting carried, but the reason it is going up here is it may be going by diffusion within a layer because in the laminar flow, the layer is very well behaved, it is going only in the direction.

So the diffusion is happening in the z direction, yeah, and then at the interface between two layers, there may be small eddies because it is two different movements, so it is like two layers are mixed at the interface, there is always some disturbances. So small eddies will carry into the next one and the next one and so on, but if there are larger eddies right here, it is diffusing, but it is also being carried to the next level by the eddies, it is happening quickly, much faster okay.

(Refer Slide Time: 11:38)

$$j_{s1} = -D \frac{d\rho_{s1}}{dz}$$

$$\rho_{s2}(\text{surface}) = \rho_{s2}^* (\text{solubility})$$

$$\eta_{h,c} = \frac{v_s \rho_s + j_{s,c}}{\rho_s} = \frac{[\rho_{s2}^* - \rho_{s2}^{\infty}]}{\text{Resistance}} = K_c [\rho_{s2}^* - \rho_{s2}^{\infty}]$$

Convective Mass Transfer Coefft.

So, how do we relate that if we want to model this using Fick's law kind of system? We have a problem because diffusion, when we are saying diffusion, I need to know diffusion is $d\rho$ A by dz , I need to know this, practically in an interface, in any interface, however and whatever system we are talking about, it is very difficult to judge. Where is that, how small is that layer and calculate accurately whether diffusion is happening here, and I can solve the equation using both advection and diffusion, problem is I need to know exactly at what dimension.

If you have a differential equation in z , I need to know boundary conditions somewhere. If I do not even know what the dimension of that, I cannot solve it. So, people do not bother about this. So, this is a very theoretical concept, but people solve it now, but when it originated, this is a surface and there is a velocity gradient, yeah. So the idea was that somewhere here below this thing, so there is a region where there is a velocity gradient that is happening right, and this velocity gradient is changing with the distance.

So, there is a region in this within surface where this influence of the surface is felt, okay, where there is a change in the velocity. Beyond this point, the velocity is uniform, velocity is whatever is approach velocity. What I mean by approach velocity is let us take this bench for example. So, there is a bench and there is air flowing. This is all uniform velocity. The moment it hit is this bench, this friction of this surface comes into play and therefore the boundary layers will start forming here.

The velocity profiles will start forming here, and there is the development of this velocity profile will be like this, initially it will look like this, very little friction is happening. Then as we go, effect of friction is higher. So, there is a region as you mark it along the thing, there is a region from the surface where the effect of the surface is felt, this is for momentum, this is for velocity. So, this is called as a boundary layer. Now, we talked about boundary layer with reference to atmospheric dispersion.

It is a boundary layer there also, but that boundary layer is a different boundary layer, it is called a boundary layer, planetary boundary layer, where it is assumed to be well mixed in. So, there will also be a boundary layer there. If you go look at it at different surfaces, there will be a small region very close to the surface where there is a gradient, beyond that, it is mixed, well mixed to a certain height and beyond that height, there is again a different profile and all that.

So, the boundary layer in atmospheric systems in earth systems are very different from boundary layers we are talking about this kind of, very close to the boundary layer also surface, there is a boundary velocity gradient and that will be there in all surfaces. You take any surface, this surface, outside, land, buildings, water. So do not confuse this boundary layer with that planetary boundary layer. The scale of planetary boundary layer is big, order of kilometers, 1 to 2 two kilometers, but this is different.

This is the hydrodynamic boundary layer, this is the flow boundary layer, momentum boundary layer okay. This is important because following this as another concept that is coming. This boundary layer marks the effect of the surface, yeah. So the assumption people make is in this region since the velocity is uniform they assume that it is also well mixed, it is may or may not be true, but the assumption is made that it is well mixed.

So, there is a region very close to the surface where the mass transfer can be a mixture of there is a little bit of convection, there is a little bit of diffusion, and depending on what is whether it is turbulent or laminar, the amount of resistance that the chemical has to move from here to here may vary, okay. So, very close to the surface, we define a region where there is mass transfer resistance. When we say it is well mixed, concentration is uniform everywhere. So, there is no gradient.

So, we do not assume there is any resistance mass transfer. There is no flux into that region at all. So, you will get used to this concept if you are not already aware of it. So, there is mass moving from here to here, there is a region in which this material is moving from here to here, and then it is mixing here, their entire region is well mixed. So you really cannot, you are then assuming that material is going from this point to this point and it is increasing, this concentration is increasing, but does not participate, there is no resistance here.

We are assuming that it is all fully mixed, okay and we take it so one. It is possible for us to even calculate gradients here, but for practical considerations, people do not consider that. They say this entire mass is one big chunk, air or water or whatever, and this is one other end of it. So, it will become clearer when we look at examples. So, because this is happening, corresponding to this we also have let us say that we have a surface that is contaminated. So, on the surface let us say I have a chemical coating, chemical coated surface, let us not worry about what is here.

So, let us say there is a thin coating of this surface here on the surface, okay. So, I can take some pure chemical and apply it on a surface and leave it and there is a fluid that is coming in this direction. So, the fluid will form start forming a velocity boundary layer at the surface, along with this fluid boundary layer, there is also another boundary layer that starts forming. This boundary layer here, the concentration of a chemical, let us say this water, concentration of the chemical at the surface will be the highest concentration.

In this case this will be the solubility or whatever we assume that this will be the ρA_2 star solubility, the highest concentration, pure chemical sitting here. So, it is in contact with water and that at that point, theoretically at this point where at the surface we will if you are writing $z = 0$, z axis is in this direction, $z = 0$ here and z is increasing in this direction. At $z = 0$, the

concentration is the highest and the highest possible concentration is a solubility, is equilibrium value okay.

So, when fluid just enters, comes in contact with this, yeah, very small region in contact with the surface will get the mass of A will transfer into that region, right. So, fluid is coming here, one parcel of fluid comes here. There is some amount of mass transfer that is happening. When it goes here, this parcel of fluid contains a little bit of A and it goes here, next it goes to the next level, it takes a little bit more. It takes a little bit more of A and so on. So, A keeps adding into this layer as the parcel keeps moving okay.

So, what will happen here is if you just like what you had a velocity gradient, you have a concentration gradient. So if I draw the concentration gradient and this is a concentration, this is ρ_A , this is scaled in this direction like the velocity, the length of the arrow indicates the magnitude of the concentration. We expect to see right here there is nothing, ρ_A to infinity let us assume it is 0, there is no A in the water that is coming towards the surface. As it approaches this surface, this part, this entire boundary layer, this is the profile, this is 0, there is no A.

As it comes to one part, this is 0 here and then it has a little bit, small amount of concentration has come now. As it goes further, there is a little bit more increase, and it goes further, there is a little bit more and so on. So, this you can form if you mark the points where the difference in concentration exists, this is called as a concentration boundary layer. This is a result of mass transfer. This is a chemical that is accumulating in a fluid as it is passing along a surface is a result of mass transfer.

This mass transfer is a result of, the way mass transfer occurs in this region is a result of this, these two are related. So, the extent of this, this Δc is related to Δv , depending on how the structure of Δv is, the Δc will change okay. So, practically here again, there is a region here where there is no concentration, it is 0 right, and there is a region here where the concentration is infinity. So, our concentration driving force can now be taken as $\rho_{A2} - 0$ which is going to be the driving force across this region, across the boundary layer.

So, this is the boundary layer across at the surface forms the region where there is mass transfer resistance and therefore mass transfer is happening through this region, and this

region is assumed to be well mixed, 0, it will not be, see it is 0, so technically speaking it is 0 and this distance is changing and all that. Again, this modeling this is not easy because the boundary layer thickness is changing and changing with high distance from the surface and all that and the description of this is very difficult.

So, very few systems where you can do this kind of nice mathematical modeling from scratch okay, from Navier-Stokes equation and equations of mass. What people generally do is this is a very convenient way of now representing, so you do not want to, I know that it is v into $\rho A + jA$ and all that, but I do not care, as long I am only interested in overall these things. So I will use the description that I have as a driving force and resistance and write down a concentration difference.

In this case, we are looking at, in this example we are looking at $\rho A_2^* - \rho A_2^0$, $\rho A_2^0 - \rho A_2^\infty$, in this case it is 0. Then I need a resistance. This resistance term is now dependent on what is going on here, in this room, this zone. So, just like the Fick's law, when you know this gradient, you can very nicely define this and this point. I can measure it and if I can measure the flux, the proportionality between these two is the resistance, inverse of the resistance okay, it is one over resistance and that is given the term mass transfer coefficient.

This is called as a convective mass transfer coefficient. This is a combination of several things, we do not care what it is at this point. At this point, it is a proportionality constant okay. Why is this important? Because if you have such a relationship, I can predict what will be the flux if I know the k and the driving force, which is what is usually our, in the box model this is what we want, we want an equation on the right hand side that we can plug into that model and take our modeling further.

So, this mass transfer coefficient is k . The mass transfer coefficient or convective mass transfer coefficient you can write different things. We will write our nomenclature terminology, this k is represented by different things in different textbooks.

(Refer Slide Time: 25:28)

$$\begin{cases}
 {}^2 k_{A1} = \text{Mass Transfer Coefficient of A in phase 1 in contact with } 2 \\
 {}^1 k_{A2} = \text{ " " " phase 2 in contact with } 1 \\
 {}^3 k_{A1} = \text{ " " " phase 1 " " 3 (Soil) \\
 {}^3 k_{A2} = \text{ " " " phase 2 " " 3 \\
 {}^1 k_{A4} \\
 {}^2 k_{A4} \\
 {}^3 k_{A4}
 \end{cases}$$

So, in our scheme of nomenclature, simply the nomenclature is k of A in a phase. Let us say this is k of A, but this is an interface mass transfer coefficient. What this means is this is a mass transfer coefficient of A in 1, the phase 1, but this 1 this interface can be anything, I can have an air-water interface, I can have an air-solid interface, I can have something else. So, I will write another number here say 2, which means phase 1 in contact with 2. So, this essentially will mean that it is a mass transfer coefficient in the air, but the air is in contact with water.

Similarly, I can write k_{A21} , this is a mass transfer coefficient of A in phase 2 in contact with air and I can write k_{A13} , this is the mass transfer of A in phase 1 in contact with 3 which is soil and I can write k_{A23} , which is the same thing but 2 and 3 which means water and solid are in contact. Which system is this? It is a mass transfer coefficient of A in water in phase 2. Water in contact with a solid, what system is that? Which interphase is that? We are talking about interphases.

These two are air and water interphase, this is soil-air interface, yeah, this is sediment water, this is sediment and water, yeah. Sediment and air does not exist unless you pull out the sediment and put it outside, it becomes soil air at that point which happens which is called as a dredge material, it is a sludge or something, which people dig up material and put it, so you will see that. So that is one, but in it is natural state, we do not do that. So, this just for our reference, so I can have a many things.

I can have anything. I can have kA_{41} , I can have kA_{42} , I can have kA_{24} , 24 means it is in contact with pure substance. For in case we have an oil spill or something, we have oil sitting there, oil is dissolving, oil is also evaporating, so different kinds of mass transfer. Because there is an interphase, there always going to be whether it is diffusion or mixture of convection diffusion, all of these things. So, this is the nomenclature we are going to be using, okay.