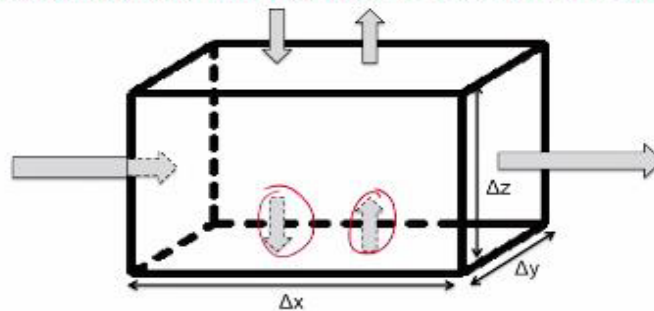**Environmental Quality: Monitoring and Analysis**
**Prof. Ravi Krishna**
**Department of Chemical Engineering**
**Indian Institute of Technology – Madras**

**Lecture – 44**
**Introduction to Interphase Mass Transfer**
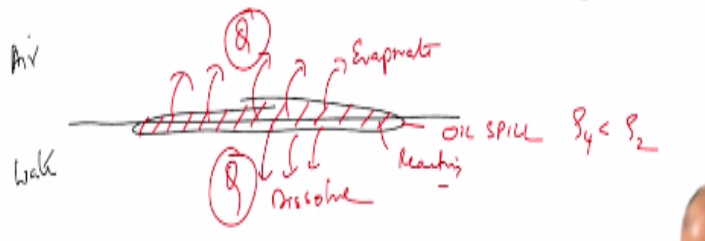
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So, in the box model one of the things that we have we discussed is you know what will happen, the dispersion modeling was a slight departure from what we are doing in the box model. So, dispersion modeling is one subset of this, we are not exactly following the box model concept in its totality. We are using the box inside a plume and then we are integrating that, but here in box model we are using it as trying to calculate for the entire system here. So, one component of this is interface mass transfer, we will discuss that.

We will discuss this exchange between interfaces. For this, we have to go and look at some fundamentals of mass transfer, okay. So, we are again taking a departure out of it. So, dispersion modeling is an entirely separate approach to doing this, we are not even looking at it this way, Dispersion is part of this, but you will see what we are discussing here based on examples that we do. Because dispersion modeling is a nice model which is already existing, so people do not mess with it, take advantage of whatever is already there.

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So let's talk about mass transfer concepts fundamentals. We will talk a little bit about fundamentals, then we will look at the application where we are okay. So what we are really interested in finding out here is again this. So, if you take the example of the dispersion model, if you need to calculate the term Q, Q is the rate of release of a chemical A from a surface which has some chemical okay. So the surface could be a water, could be soil, could be anything okay.

In the case of rivers, rate of release, this is in a dispersion model, Gaussian dispersion model we will use this, but in the case of a box model, you are also using this term rate of release of A from a surface or rate of removal to a surface. So we have air to water, we have water to air, we have air to soil, we have soil to air, then we have sediment to water. So a lot of these scenarios exist. So for example simple examples of this say we have water, we have air, and here we have an oil spill let us say we have an oil spill, okay. If you assume that the oil has a density, $\rho_4$ which is less than that of water.

The density of the oil is less than that of water, it will float on water okay. When it floats on water, depending on the composition of the oil, some components will evaporate and some components will dissolve. So, if you want to know what happens to this oil spill over a period of time and what is its impact in the environment, you need to calculate how much is evaporating and what is the rate of evaporation and what is the rate of dissolution into this.

This information will give you how long if I just leave the oil spill without doing anything what is going to be the impact. You also determine whether if you do not do anything, what will

happen? This is an option sometimes because doing something will cost a lot of money, so people will say I will not do anything, leave it there. it Its impact is not going to be great, it will just go away okay and it can also react, so degrade it can also degrade which means there is reaction that can happen.

It can also divide itself into smaller spills. This bigger large spill will break up into smaller components and it will float around, it will spread, all those things can happen, we will discuss that again. So, this is calculation of this Q here is what we are thinking about.

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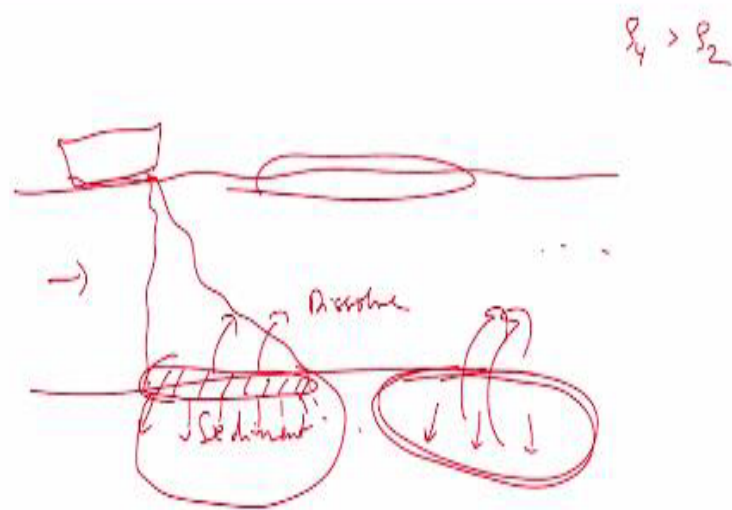


Another example of this is, I have a boat that is carrying a lot of chemical, there is sediment which is under water, we had discussed this. The density of the chemical is greater than that of water, then it will not float, it will sink. It will sink down to the ground. So if you are in a river, it will sink and it will occupy a region at the bottom on the bed of the sediment. So, when it occupies this region on the bed of the sediment, what will happen to this chemical that is sitting here, it can dissolve, yeah, but it can also spread in the direction of flow in the sediment.

So, if you spill say a 1 ton of chemical and it goes all the way down and spread down on the river bed, you come back after 2 years, this will become like this. The extent of contamination will now extend downwards into the sediment, so over a period of time, it will go. So, how does it go? How does it spread? Once it spreads down, then it is again started releasing itself. This starts reversing its direction to go out. So, these are all things that happen over a very long timescales and people do not see it because it is not visible.

If the oil spill on the surface, it is very visible, you can see, everybody can see. Suppose it is a chemical, you cannot see, it is down there somewhere, you cannot see it unless it comes into the water. There are a lot of cases where it has come into the water over a period of time, a long period of time and the only way to monitor it is you have to go down and see what is there in the bed of sediment.

So, this is one other thing. So in this context, you are also interested in seeing how is it moving inside. So that's not interface mass transfer, but it is mass transfer in a different way. So these are some of the cases and then of course there is soil and air.

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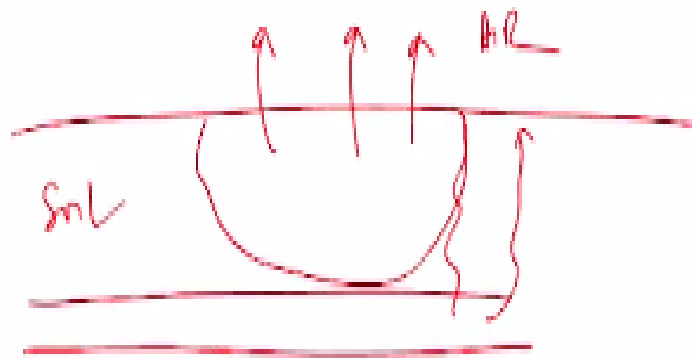


So you have soil. This is a very common thing. You have soil and there is contamination, there is a spill and it releases to air or there is a pipeline underneath and that is a spill there and then chemical escape, evaporate through this and then come out, all this these are all transport problems okay. So, I want to give you a brief overview on the transport fundamentals, it will probably take one or two lectures on this, where it is easier for you to appreciate how the calculations are done.

Some of you have already must have seen it in some other course, so it is just a refresher, for some it may be new, so we will try to cover as much as possible fundamentals of mass transfer system.

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FUNDAMENTALS of MASS TRANSFER
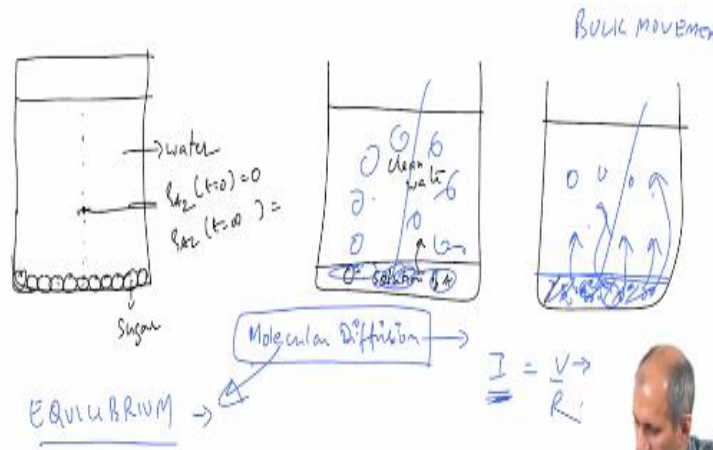
So, essentially, we start with the mass transfer itself. If I put in a bottle, take a jar of water, then I put a chemical underneath at the bottom. Let us say that I put some crystals of salt or sugar right here in the bottom and I fill this up with water okay. Now what one expects here is this this say sugar, let us assume it sugar for the time being okay, and I am just leaving it, I leave it just like that, I do not disturb the water at all. So normally what would you do if you want to mix sugar, you want to dissolve sugar into water? What is your normal thing is to stir it.

Why do you stir it? Why do you stir it? What is the purpose of stirring? If you do not know mass transfer and you are not chemical engineer, why do you stir it? Dissolve it, but how do you know that it will dissolve? If you don't stir it and stir it, what is the difference? Entire mass is mix when stirring. Yeah, practically why would you stir it? Uniformity. Uniformity is one, something else more fundamental. Faster. It is faster, so somehow you know that it is faster okay?

So, dissolution is faster when you stir it okay. When you stir it, you are making sure it is faster. So if I do not stir it, will there be no dissolution at all? There will be. You people are from chemistry background, so you are chemistry right, have you seen this concept of mass transfer before? You have studied diffusion and all that, you should have studied in physical chemistry okay. If you do not stir it, will there still be transfer? If I want to measure the concentration of the sugar in the water, initially the water is all clean, will there be mass transfer at all?

Will the concentration, so let us say the concentration of sugar at time $t = 0$ is 0 at this height, let us say at this height. Say at time t equals some 10 hours, this concentration would you expect

without mixing, if you do not mix this water, would you expect it to be nonzero or zero? Let us say 10 hours or let us say infinite time, 100 hours, 2000 hours, sometime long, just forget about it and come back after 100 years, would you find some concentration nonzero, yeah, but nobody has mixed it okay.

So why would a chemical move from one place to another place if you are not mixing it. So mixing it is very intuitive. You are taking this chemical, so let us take the case, sugar is a very bad example in this. Let me give you another example where sugar has to dissolve right. Let us take I already have a dissolved solution. I have a dissolve solution of sugar and I have plain water on top, no mixing, I put one on top of the other okay. This is also a solution of A, this is clean water, will A move, forget about dissolution and all that, will A move when you do not mix it.

So, when you are mixing when you are mixing it, you are taking this portion, you are taking portions of this, these portions are going into the bulk of the water and you are facilitating the mixing process. When you do not do that, when you leave it as it is when you leave it as it is, do you expect the water layer to, do you do you expect the solute in this to mix, to move here? The answer is yes and the process by which it moves is called as molecular diffusion and this is fundamental to all mass transfer.

When you take a spoon and mix it, you are really mixing, you are physically taking the mass and putting it somewhere else, it is not in the same class of mass transfer as we are doing molecular diffusion. Molecular diffusion, why does the chemical want to move from here to here, you are not giving it any energy, you are letting it sit there. Why will a die or some solution here, you can see this in in examples where you have one solution which is colored and one clean water.

You can see over a period of time this color thing will move, it will slowly move, you can see that, so why will it move? Moves by molecular diffusion, but why does it move by molecular diffusion? Because of chemical potential. What is chemical potential? So chemical potential is the thermodynamic reason. So, like all things in all other systems, there is a potential difference for it to move. So, if you take Ohm's law, this is a rate, this is the potential difference, this is the resistance, this is a universal law.

You take some other law for a Bernoulli equation or something or Darcy's law, any such thing, all of them are the same format, rate equals potential difference divided by resistance okay. So, what is the potential difference here? This chemical potential difference is not exactly but crudely can be approximated to concentration, but why does it want to move? Concentration difference itself, why does it cause something to move? So very, from a thermodynamic point of view, why does it move?

Entropy, randomness. What is entropy? What happens to entropy? What is the meaning of entropy in this system? From a molecular point of view, everything is trying to go from one state to a state where it has   more freedom, it is not stability.

Let us say that you are entering a you are entering a, I do not know, it is a bad example, but let us say you are going to a movie theater, and watching a movie. No seats are assigned to you; you can sit wherever you want. Where you will go and sit. It has all strangers; you do not know anything about them. There is one group of people sitting in one corner, where will you go and sit? Yeah. You will go and sit in some place where it is free. If 4 people come and sit next to you, you will go and move to another place where it is less crowded.

So this is observed in all systems. People migrate, populations migrate because of this. One place becomes very crowded, they cannot stay there, they will go, they will spread. What it is, it tries to find the system where there are more degrees of freedom, you have more freedom in terms of you are not constrained, so it tries to find a system where there are maximum, at some point it cannot go anymore, it will everything is the same, all confirmations are the same, it will stop there and that is equilibrium, but there are other energy aspects to this.

So from that point of view, this wants to move to a point where there is more freedom, so it crudely translates to a region of higher concentration to a region of lower concentration, but it is it is just simply not concentration. It is the chemical potential in equilibrium because in this particular case, it is uniform concentration because they are all in the same phase. This is water, this is also water, it is moving in water, but if you take a chemical which is volatile, for example if I take naphthalene or something or benzene in water.

And I keep it exposed to air, all the benzene is not going to enter the air and become uniform concentrations. It is going to reach a value where they are not the same but it will not go

anymore. So, from that context chemical potential is not just exactly concentration that is why the definition of concentration and chemical potential are reference to this equilibrium is different. So, this is related to what is called as equilibrium. So equilibrium is a state where the chemical potentials are same, which means that there is no further change in any degrees of freedom it's all.

They have reached a state there, that is it, it cannot go anywhere else and it is now does not want to go anymore. Until there is no there is equilibrium, there is a non-equilibrium state, there will be transport, mass transfer. Now that is molecular diffusion okay. What we do when we mix, we take a spoon and mix this water, mix the solution, it is not molecular diffusion. We are doing what is called as bulk motion, bulk movement.

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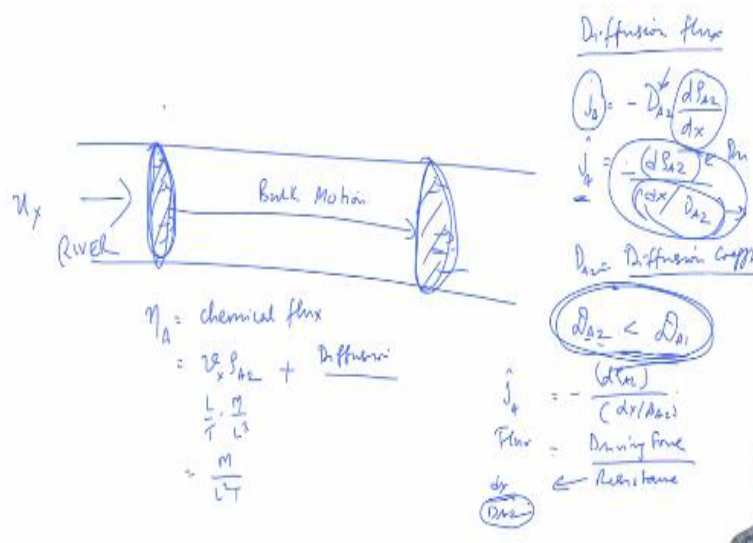
For example, let us say that I have a river and I dumped a kilogram of a chemical here. This kilogram of chemical moves here downstream. It is moving. There is a rate at which it has moved okay? There is a flux based on that. What is the rate at which it is moving? This velocity of this river water is Ux, it is moving at the velocity of the river that is all. It is non-interactive, it just moved as it is, similar to this dispersion in Gaussian dispersion model, its mass is taken by the air and goes from one place to another place.

So it is not molecular diffusion. Is molecular diffusion happening in this, no? Yes, it is always happening. Molecular diffusion is always happening, but the predominant is bulk movement. So for example molecular diffusion happens. So, if the mass, this is the boundary of this chemical here, by the time it reaches here, maybe it will become like this, slightly bigger

because molecular diffusion also is happening along with it. So, this we introduced a term called as flux, chemical flux.

The reason we do flux instead of rate is that you know we can normalize it by area and area can always be added, the reasons will become clear later, but the flux is an easy term to work with. So, the total flux, this is called as bulk motion. This velocity is responsible for moving this piece of chemical from one place to another place. So, if you calculate the flux of this chemical from point 1 to point 2, how is it moving? What is the total flux, velocity multiplied by the concentration in the water.

So, if you look at the units this is L/T, this is M/L$^3$, units will be $\frac{M}{L^2 T}$, this is unit of flux, yeah, plus diffusion. Now what is diffusion, flux by diffusion. So, in the system that we described people have studied this a lot in chemical engineering as well as other disciplines. They put something, in the experiment that I have described, they put something there is no mixing, but they still see things are moving across, a very classic experiment.

They put a gas on one in one bulb and another bulb is free, and they see how much how quickly it moves from one to the other and all that. So without any mixing, without any bulk motion, which means you are not pushing air, you are not pushing water, you are just leaving it, very difficult to do by the way. You imagine very difficult to keep something that, set up the experiment itself is very difficult. Theoretically, we told you that if I can add one layer of colored liquid and on top of it place one layer of water, it is not easy to do okay.

The process of adding water itself everything mixes, there is bulk motion because you are pushing, you are providing some external energy and it is always going to move, okay. So diffusion flux people have studied and it takes the same form as heat flux, heat flux is a law called Fourier's law, the same form diffusion flux we call it, give it the term Ja differentiate it from the bulk motion and it is described as in this case, we will describe as this, just rho A2 by dz, dx o dx whatever, in this case it is dx.

$$j_A = -D_{A2} \frac{d\rho_{A2}}{dx}$$

$$j_A = -\frac{d\rho_{A2}}{dx/D_{A2}}$$

So, we are looking at this transport in this direction, in x direction, it can be any direction, does not matter. So, what this does essentially is if you look at this, this is a flux term, this is diffusion flux. If you split this, it is in essence this is a takes the same form as your i equals vr, this is the flux, i equals vr current that is a flux of electrons, the flow of electrons the flow and this is a concentration driving force, this is a difference in concentration, effectively from chemical potential we are converting to concentration and this bottom is a term called $dx/D_{A2}$.

So, generally what people found is that this this term, the flux is proportional to the gradient, the extent the magnitude of the gradient, the larger the gradient, more transport is occurring. So, this term DA2 is a proportionality constant, this is called as diffusion coefficient. This is a proportionality constant, at that initially it was just a proportionality constant, subsequently people learnt more about that and have correlations for it. You can derive it from molecular theory for large sized molecules, it is called as Stokes-Einstein equation, you can derive it as there is a well-formulated system for it.

So you will get the actual form from atomic theory, molecular theory, but in the beginning as it happens with most of the cases people took it as a proportionality constant and then they figure out what is this number dependent on, what it is a function of, what properties of the chemical or what properties of the medium and all that. So diffusion coefficient is a proportionality constant, so higher the diffusion coefficient, higher is the flux for a given gradient or vice versa.

You have different gradient for the same diffusion coefficient, again flux is going to be different. So, two parameters here that that are that are important. So, the diffusion coefficient, we call it our nomenclature in following whatever we are doing in the course, diffusion coefficient of A in water. Suppose you are doing this for air, DA1, so the diffusion coefficient in the form that you are writing it like this, what is this denominator term represent? This is a driving force, yeah, so,

$$j_A = -\frac{d\rho_{A2}}{dx/D_{A2}} = \frac{Driving\ Force}{Resistance}$$

So, the resistance is dx by DA2, which means that higher the value of DA2, lower the resistance, yeah. So what do you mean by resistance here from a molecular point of view, this is molecular diffusion, what is this resistance, diffusion coefficient is inverse of resistance. So, if DA2 and DA1 which one do you think is more for a same chemical. So, diffusion of benzene through air or diffusion of benzene through water, which one will be more. DA1, whyDensity. Density more means what happens, if the density is greater in water.

More density will provide more resistance. More resistance in the form of Molecular interactions. Molecular interactions are higher. So essentially something like a drag, if you have more more interaction, more interaction more molecules, more density of molecules, which means there is greater interactions and therefore greater drag and all that. So, this is one of the reasons why this is higher. So, it is a function of this is 3 to 4 orders of magnitude difference between diffusion coefficient of 2 and 1. I think we stop here.