Course: Adsorption Science and Technology: Fundamentals and Applications

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Week 04

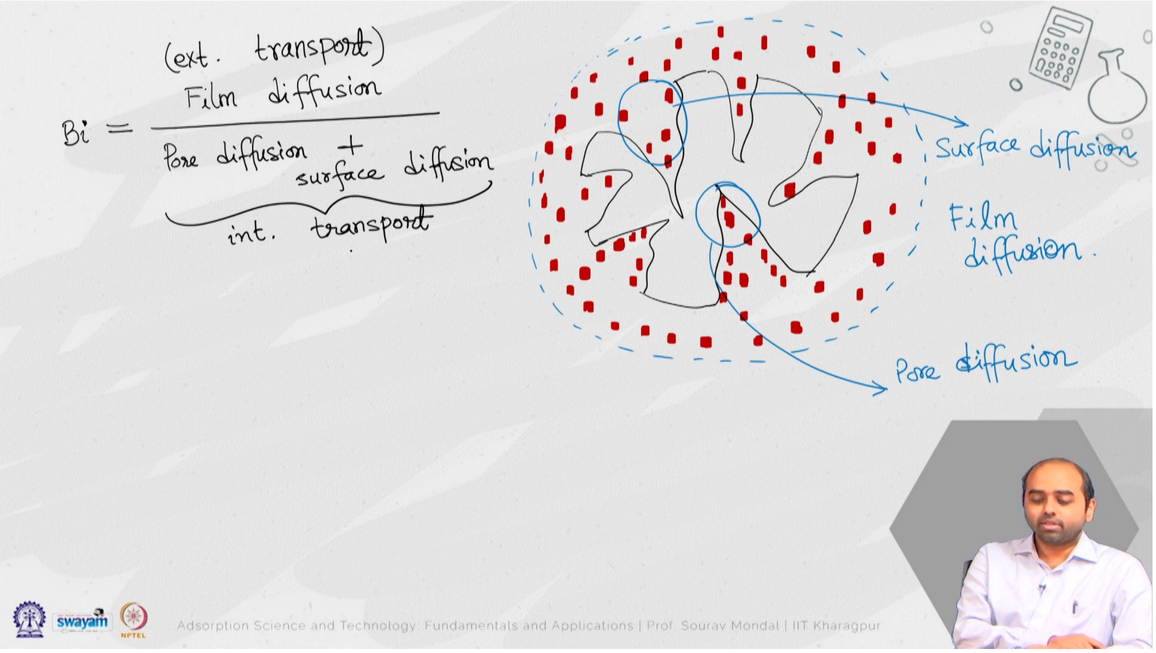
Lecture 17 | Film Diffusion

Hello everyone, welcome to this class on adsorption science and technology. Today we are going to talk about this flim diffusion. So, in the last class we have seen that we talked about how diffusion plays a very important role in the overall mass transport phenomena during this process of adsorption. And often diffusion affects significantly on the rate of transport particularly the intrinsic transport. And there are various types of you know diffusion which can affect the you know overall transport rate particularly in the context of pore diffusion, then you have you know bulk diffusion or inter particle diffusion and often these diffusion steps can be rate limiting in nature particularly for adsorbates present in the liquid systems. In the gas case, generally diffusion is much faster.

So, often these resistances are ignored and it is primarily governed by adsorption. But in the case of liquid systems where the adsorption happens in the liquid phase, these resistances becomes very important. Now, coming to this aspect of film diffusion it is very important to understand that what are the different factors on which this film diffusion are at what scale or what is the you know different types of physics where this film diffusion actually does play a big role. By film diffusion we mean that typically the diffusive nature of the particles or the adsorbate species follow Maxwellian you know diffusion behaviour which is described by the Fick's law of diffusion.

So, particularly in the liquid phase the mass transfer depends on several factors and it could be a combination of you know various types of liquid phase flows, it could be mixing conditions, it could be intra particle or inter particle conditions. It could be your, you know, film diffusions which all of them pose overall, you know, significant resistance to the overall rates of this transport. So, just to give you a quick schematic, you know, representation of the overall rates of the diffusion. So, let us consider that your particle, adsorbent particle looks something like this where you have different pores in the particle. Of course, this pore mouths are actually open to the bulk.

So, I should draw this properly and neatly to avoid any confusion. So, it is like this. Something like this. Now we have the adsorbate species in here which is let us say you know coming on the surface of this adsorbent particles and creating a film. So this is mostly the surface diffusion or let us say the fluid film diffusion engulfing the particles and then we also have diffusion inside the pores which is again of two types.

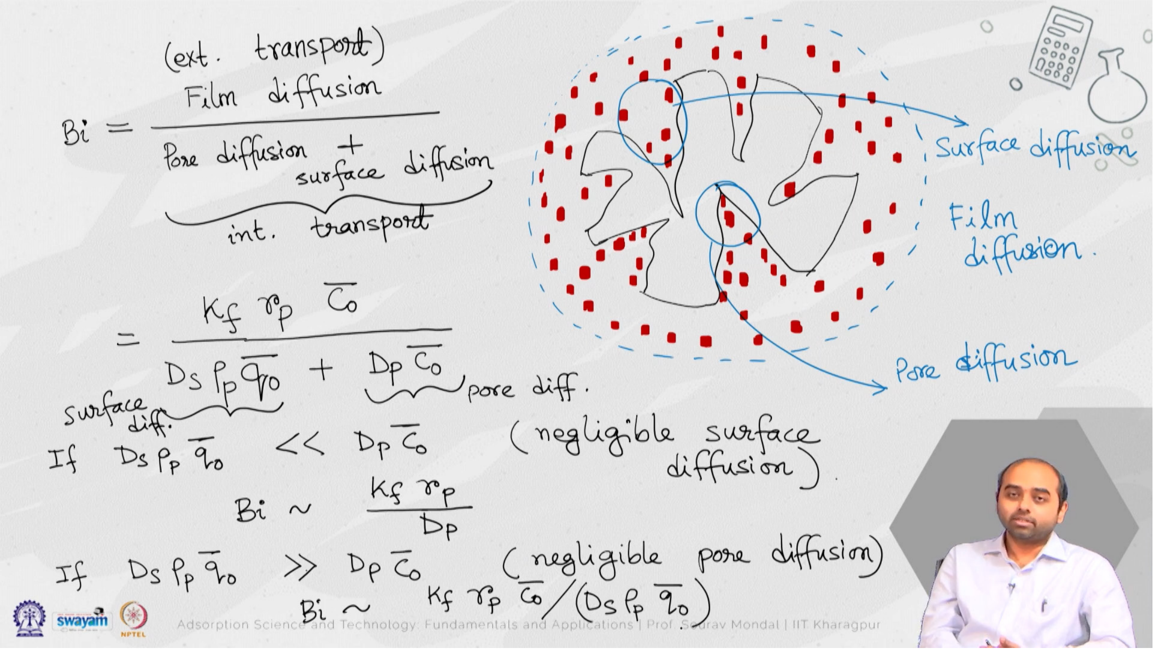


$$Bi = \frac{\overset{\text{(ext. transport)}}{\text{Film diffusion}}}{\underbrace{\text{Pore diffusion} + \text{surface diffusion}}_{\text{int. transport}}}$$

So one is like pore diffusion where the particles move towards or insides of the pore and another is of course, the surface diffusion inside the pores. So, the pore diffusion is primarily affected by Knudsen diffusivity and surface diffusion again inside the pores particularly for high porosity particles is described by the Maxwellian nature where the you know pore dimensions are much larger than the mean free path length . So, if you try to you know segregate these different types of diffusion. So, this is what is referred to as the liquid film or the film diffusion inside the pores. This is what is referred to as pore diffusion and within the pores particularly on the surface of the pores is referred to as surface diffusion.

So, I must emphasize once again that this diffusion is particularly important or rate limiting in liquid systems where the diffusive resistance is much could be comparable or higher compared to the overall rates of transport in the adsorption. So, for gases this is not a very big deal particularly film diffusion resistance for gases is not at all important it is mostly the pore diffusion resistance. At least from the different types of diffusion resistance the contribution from pore diffusion or the resistance from pore side is maximum from from the gas phase. But for liquid phase all of this is very important and the particular way to quantify all of these parameters it be to designate the biot number in this case. So, the Biot number in this case is defined by the rate of Film diffusion which is mostly caters to the externals transport, divided by the rates of pore diffusion plus surface diffusion inside the pores.

Both of these two accounts for the internal transport here. So, the relative importance of the internal transport with respect to the external transport is what essentially one means by the Biot number that many of you may be you know accustomed to in the case of heat transfer particularly where the lumped parameter based approach is generally consider when a distributed based parameter approach is necessary. So, again in this case here also in the case of you know this pore diffusion or when the diffusion resistances inside the pores becomes important compared to the external diffusion. It is necessary to have a you know distributed parameter approach to solve the problem rather than a lumped parameter system where we do not consider what is happening inside the particles and it can be ignored and the essentially the transport or whatever this overall or the averaged mass transport or the adsorption rate inside the particle is good enough in that case to be considered on the overall dynamics of the problem. So, now this can be quantified the rate of film diffusion here can be quantified with respect to the classical you know Sherwood number formation something like mass transfer coefficient multiplied with diameter or the radius of the particle multiplied with the bulk concentration.



$$Bi = \frac{\overset{\text{(ext. transport)}}{\text{Film diffusion}}}{\underbrace{\text{Pore diffusion} + \text{surface diffusion}}_{\text{int. transport}}}$$

$$= \frac{K_f r_p \overline{C_0}}{\underbrace{D_s \rho_p \overline{q_0}}_{\text{surface diff.}} + \underbrace{D_p \overline{C_0}}_{\text{pore diff.}}}$$

If $D_s \rho_p \overline{q_0} << D_p \overline{C_0}$ (negligible surface diffusion)

$$Bi \sim \frac{K_f r_p}{D_p}$$

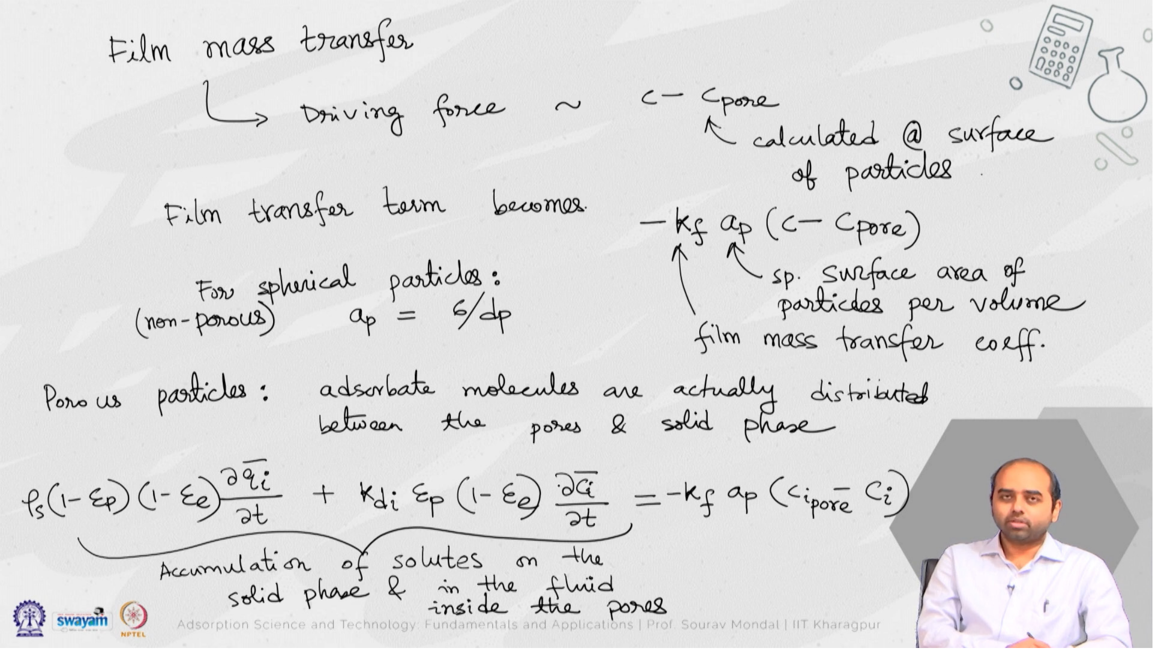
If $D_s \rho_p \overline{q_0} >> D_p \overline{C_0}$ (negligible pore diffusion)

$$Bi \sim K_f r_p \overline{C_0} / (D_s \rho_p \overline{q_0})$$

So, we assume that the surface concentration is very small in this case and this can be easily written down with respect to the surface you know diffusion. On the denominator for the pore diffusion as well as for the surface diffusion components we write both of them. Thank you. So these two are the contributions from the pore diffusion and the surface diffusion. You can particularly as I can write this as like bar.

So these are like averaged quantities. So one can see that what happens in the case of the surface diffusion. So there are different cases when one of these diffusion rates is much higher compared to the other. So for example if So, this suggest negligible surface diffusion. So, this is the component of the surface diffusion on the solid surfaces inside the pores and this is the contribution with respect to the pore diffusion.

So, in that case the Biot number expression simplifies to, where Dp is sort of the Knudsen diffusivity for this system. In case if this surface diffusion is larger than pore diffusion. sorry this is pore diffusivity multiplied with C0. So, in this case negligible pore diffusion or the pore diffusion resistance is much smaller compared to the surface diffusion. The Biot number in this case is simplified to the rates of mass transfer coefficient for the film diffusion divided by the surface diffusivities and the you know the average rate of adsorbate concentration in the solid phase.



Film mass transfer

$\hookrightarrow$ Driving force $\sim$ $c - c_{pore}$ $\leftarrow$ calculated @ surface of particles

Film transfer term becomes $-k_f\, a_p\, (c - c_{pore})$

k_f $\leftarrow$ film mass transfer coeff.

a_p $\leftarrow$ sp. surface area of particles per volume

For spherical particles: (non-porous) $a_p = 6/d_p$

Porous particles: adsorbate molecules are actually distributed between the pores & solid phase

$$\underbrace{\rho_s(1-\varepsilon_p)(1-\varepsilon_e)\frac{\partial \bar{q}_i}{\partial t} + k_{di}\,\varepsilon_p(1-\varepsilon_e)\frac{\partial \bar{c}_i}{\partial t}}_{\text{Accumulation of solutes on the solid phase \& in the fluid inside the pores}} = -k_f\, a_p\,(c_{i\,pore} - c_i)$$

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So, particularly if the surface diffusion is negligible then in that case the pore diffusivities could be controlling or the relative effects of the you know this flim diffusion with respect to the nodes and diffusivity and this is what we are more you know used to in comparison to sort of the working out what would be the you know this Biot numbers in this case the Biot number takes almost the form of the Sherwood number in this case. But whereas in the case of this negligible pore diffusion the rate of adsorption becomes very important and in that case the relative you know this quantity this has represented the bottom you can see in the screen this mass transfer coefficient etc., with respect to the you know the surface diffusion coefficient as well as the amount absorbed q naught of the average amount absorbed becomes important or significant. Now let us try to look into the scenario when we have you know overall transport system both inside the pore as well as outside the pore.

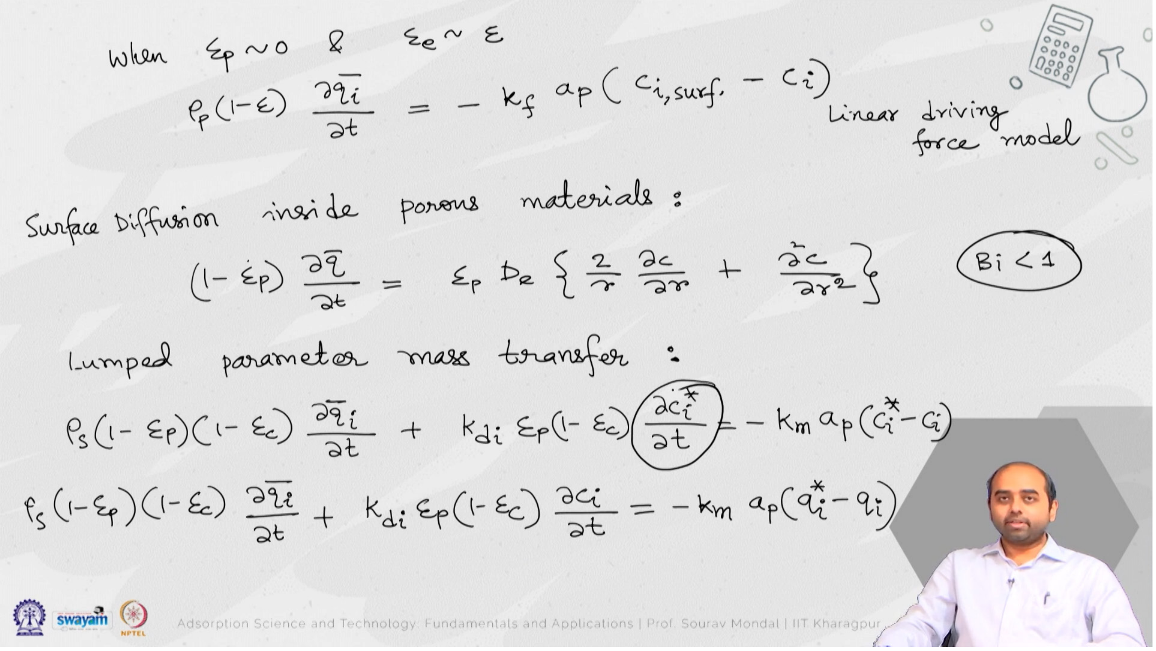
So typically this. When you do a mass transfer analysis it is important to realize particularly for film based mass transfer. The driving force is the bulk concentration minus the pore concentration where the pore concentration is actually calculated at the surface of particles is like the exit of the pore. The film transfer or the mass transfer term becomes mass transfer coefficient multiplied with the specific you know surface area of the particles per volume and the difference between the concentration or the driving force. So this represents the specific surface area of particles per volume. So, many a times this needs to be you know multiplied with the or divided by the density to take into account for generally the surface area which is available in terms of you know this in terms of the mass of the adsorbent.

So, many a times that needs to be divided with respect to the density to get the specific surface area and kf is nothing but the film mass transfer coefficient. And this is can be estimated from the Sherwood correlations that we have already discussed in the previous class. Now for spherical particles of course ap can be related to something like this, but here we are considering that for non porous particles, but for porous particles the surface area will be different. Now, it is important to note that the accumulation for porous particles it is important to note that adsorbate molecules are actually distributed between the pores and the solid phase. So the internal mass transfer is in slightly again split into two parts and that is what we have already seen in the description of the Biot number.

So naturally the mass transfer relations that is I mean written down in this case the species balance equation. Again has contributions from two parts one is from the surface diffusion inside the pores and one is from the you know pore diffusion with respect to the outside film transport. So the resulting mass transport equation looks something like this. So, in the left hand side of this equation this has accumulation of the solutes accumulation of the solutes on the solid portion or the solid phase and in the fluid portion inside the pores. I missed one more term that typically if use there will be one more term here.

Let me write it properly. So there are two types of porosity I have defined both inside the pores. One is the porosity of the you know particles that is epsilon P and one is of course the porosity inside the fluid or the fluid phase or the solid phase which is defined as the epsilon e because we are really looking into inside of the particles. So, particularly you can understand that if you set this epsilon p to be 0 and epsilon e to be like epsilon, then it can get to be a single porosity model. So, I will once again before going into the simplified version I would like to emphasize that here you have contribution from two parts.

One is that the accumulation term in the solid phase which is represented by the first term on the left hand side and one is the accumulation term from the fluid phase which is the contribution from the second term on the left hand side. Now, for scenarios you know when epsilon P is 0 and epsilon E is set to epsilon then this previous equation you know is simplified to something like this. So, the entire you know the diffusion inside the pores is actually gone. Because we are ignoring the pore you know porosities in that case and in that scenarios this becomes like at the surface of the particles. So, this is a very popular model and is known as the linear driving force.



when $\varepsilon_p \sim 0$ & $\varepsilon_e \sim \varepsilon$

$$\rho_p (1-\varepsilon) \frac{\partial \bar{q}_i}{\partial t} = - k_f \, a_p \left(c_{i,\text{surf.}} - c_i \right)$$

Linear driving force model

Surface Diffusion inside porous materials :

$$(1-\varepsilon_p) \frac{\partial \bar{q}}{\partial t} = \varepsilon_p D_e \left\{ \frac{2}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2} \right\}$$

$\boxed{Bi < 1}$

Lumped parameter mass transfer :

$$\rho_s (1-\varepsilon_p)(1-\varepsilon_c) \frac{\partial \bar{q}_i}{\partial t} + k_{di} \, \varepsilon_p (1-\varepsilon_c) \boxed{\frac{\partial c_i^*}{\partial t}} = - k_m \, a_p (c_i^* - c_i)$$

$$\rho_s (1-\varepsilon_p)(1-\varepsilon_c) \frac{\partial \bar{q}_i}{\partial t} + k_{di} \, \varepsilon_p (1-\varepsilon_c) \frac{\partial c_i}{\partial t} = - k_m \, a_p (q_i^* - q_i)$$

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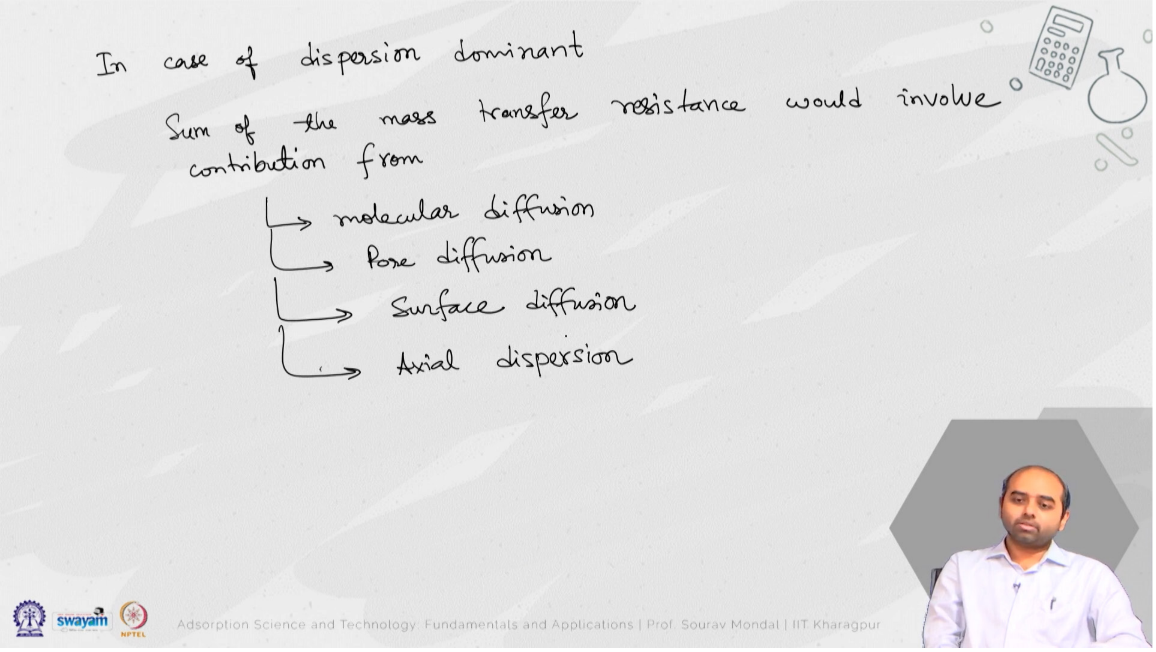
We will talk about this more in the you know next lecture, but just to give you a quick overview of how does it look like. Of course, inside the particle inside the particle if the solutes diffuse. So, inside of the particle if the surface solids diffuse which is particularly accounted for by the you know diffusion or the surface diffusion then that is something we have already talked in the previous class. So, the diffusion inside the pores or diffusion I would say surface diffusion inside porous materials particularly on the solid phase is represented by this and this is something we have already talked in the previous Last. But this is particularly for the system when we know that you know the inside or this needs a distributed parameter approach or when the you know Biot number is essentially small.

For large Biot numbers it is more of the lumped systems and we do not need to analyze the scenario where inside of the particles what is happening and entire thing can be considered or attributed to as an overall you know lumped systems. Similarly, in the case of I mean let me write down what happens in the case of lumped parameter mass transfer models. In this case we will have you know the two driving force one is the concentration difference and one is the difference in the adsorbate concentration in the adsorbent phase. So, naturally these two would also be in equilibrium inside the particles. So, the resulting equations that one would get in that scenario.

Can construct the equation like this. So this is the scenario when we have the driving force as the difference in the concentration. And in other case we also have a similar situation when the driving force is the adsorbate concentration difference in the solid phase. So the only difference between the left hand side of these two expressions is that in the first one the species concentration C i star is in equilibrium and this is the scenario we are talking about when the concentration inside the particles is in equilibrium and the driving force is the difference of the equilibrium concentration with respect to the free or the far away concentration. Whereas, in the second case where the driving force is actually the difference of the adsorbate concentration or particularly in the surface domain the rate of accumulation need not to be at the equilibrium so these are the two different you know lumped parameter based systems of course this can be reduced to a single parameter system for simplicity but this is the scenario when we have you know lumped approach where we do not track what is the level of concentration inside the particles, but rather we consider the effect net effect of the concentration both in the solid phase as well as in the liquid phase and the overall resistance is actually summed up with the linear you know this driving force in this case.



In case of dispersion dominant

Sum of the mass transfer resistance would involve contribution from

- → molecular diffusion
- → Pore diffusion
- → Surface diffusion
- → Axial dispersion

Just before we finish today's lecture I just wanted to tell you that in the case of dispersion when dispersion is dominant in the case of, so dispersion dominant so this is particularly relevant in fixed paid systems which will something see in the next week actually. The overall sum of the resistance the sum of the mass transfer resistance would involve contributions from molecular diffusion then you have pore diffusion surface diffusion as well as axial dispersion. So, there would be contributions from all of these different terms and the bed porosity and the you know this bed permeability can also play a big role or the packings in the bed can also play a big role because axial dispersion is influenced by convection. So, with this I would like to close today's lecture. In the next class we will talk about the linear driving force law in much more detail and we will tell you how this is constructed and how it is solved under simplifying scenarios.

Thank you. I hope all of you found this lecture useful. Thank you.