Course: Adsorption Science and Technology: Fundamentals and Applications

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Week 04

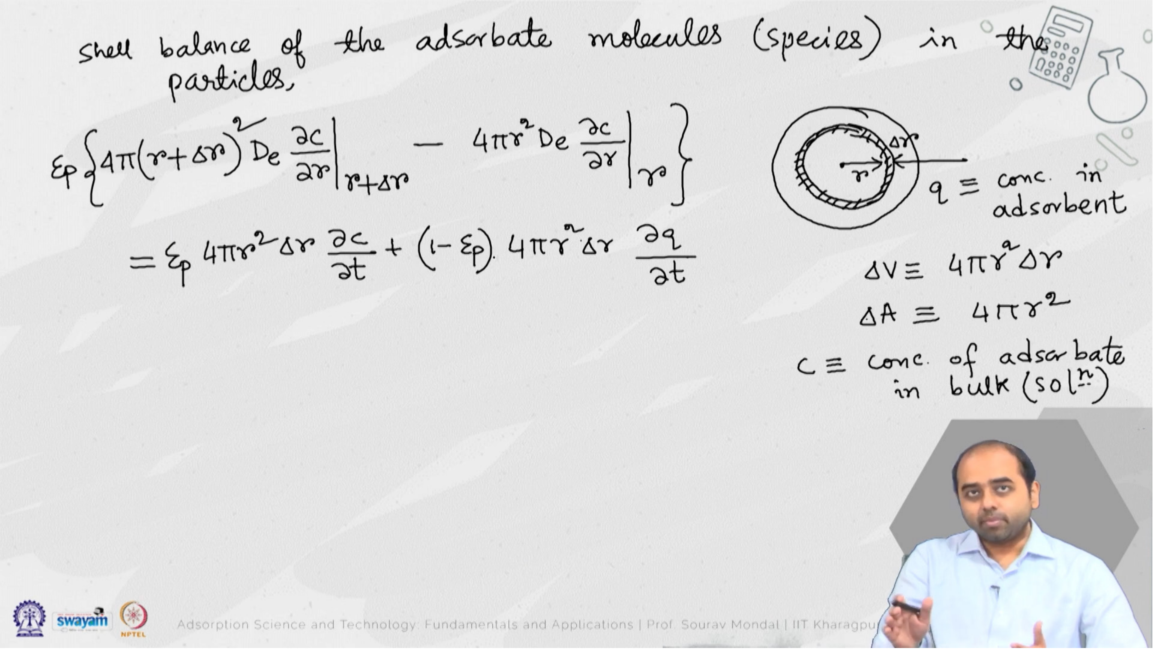
Lecture 19 | Intraparticle Adsorption Diffusion Model

Hello everyone, in this class we are going to talk about the details about intraparticle you know transport that happens within a particular spherical particles and this is a particularly relevant phenomenon since the major or the actual adsorption happens inside of these particles. Particularly, in on this adsorption happening in the bulk in the dispersion phase or in terms of the packed bed which we will probably look into in the next week the class. This adsorption inside of these particles does play a big role and often this could be the rate limiting step of the entire process. So, it is very important to study and understand what happens in the intraparticle level of the transport or within the particle where simultaneously diffusion and adsorption takes place. So, let us try to understand this intraparticle diffusion model where adsorption does also play a big role simultaneously along with diffusion. So, typically the we are going to make a shell balance, this shell balance of the adsorbate of the adsorbate molecules in the particles.

So, let us assume a spherical particle and let us consider a small control volume section of delta r thickness. This is the control volume across which we are going to do this mass balance of the shell. So, this control volume is located at a distance r from the centre. So, in this case the diffusive flux across this.

So, we are going to make the shell balance where mass in minus mass out is equal to the rate of you know this accumulation with time as well as the rate of this appearance or disappearance due to the adsorption. So, this will be r plus delta r this d diffusivity, then we will be having del C del r. So, this is the diffusive flux at r plus delta r, we will have the you know this value at r. So, this is at r. Now, this is this entire thing this transport of the diffusion flux is happening within the porous region.

So, this will be multiplied with epsilon p that is the porosity of the particle. On the right hand side we have the accumulation term. So, that is 4 pi r square delta r. So, this is the small volume of this control segment. So, this volume delta v here of this small control volume is the surface area 4 pi r square multiplied with the thickness delta r that is how you may get the volume of this small elemental segment whereas in the case of this flux the diffusive flux is multiplied with respect to the this value at.



Shell balance of the adsorbate molecules (species) in the particles,

$$\varepsilon_p \left\{ 4\pi (r+\Delta r)^2 D_e \frac{\partial c}{\partial r}\Big|_{r+\Delta r} - 4\pi r^2 D_e \frac{\partial c}{\partial r}\Big|_{r} \right\}$$

$$= \varepsilon_p 4\pi r^2 \Delta r \frac{\partial c}{\partial t} + (1-\varepsilon_p) 4\pi r^2 \Delta r \frac{\partial q}{\partial t}$$

$q \equiv$ conc. in adsorbent

$\Delta V \equiv 4\pi r^2 \Delta r$

$\Delta A \equiv 4\pi r^2$

$C \equiv$ conc. of adsorbate in bulk (sol^n)

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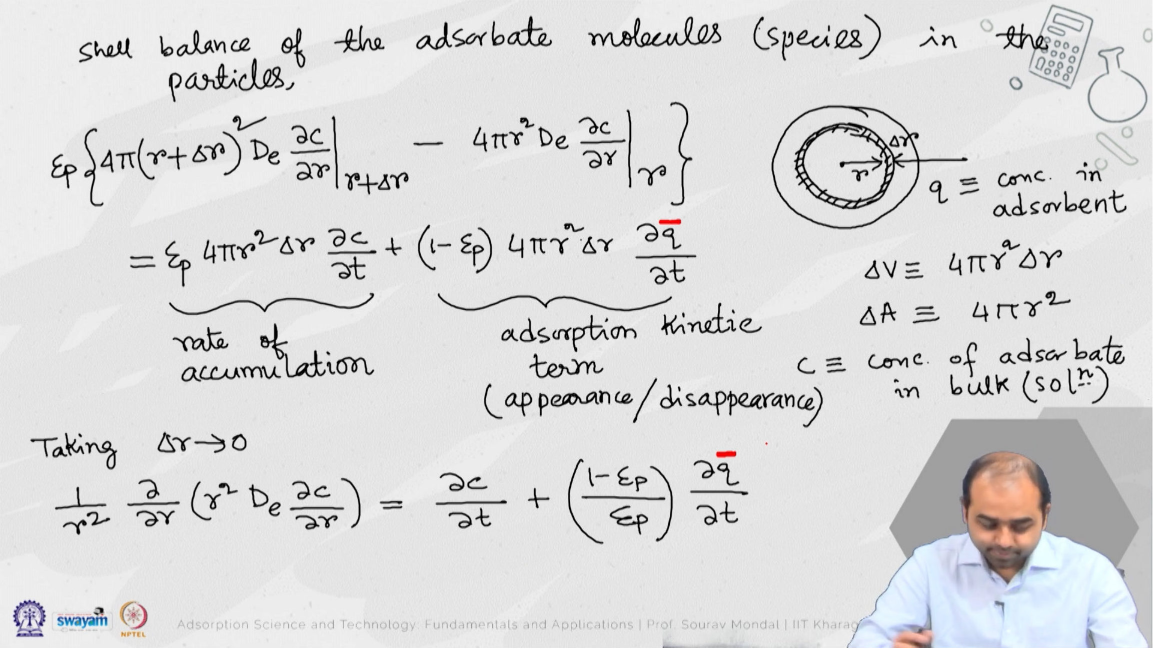
So, this surface area is 4 pi r square. So, this will be squared. So, this is 4 pi r square delta r multiplied with dC by dt. So, here please note that C is the concentration of adsorbate in bulk or solution. and q refers to the you know the concentration of the adsorbate in the solid phase.

So, this would be again multiplied with epsilon p and then we will have the same term 4 pi r square delta r dq by dt where q represents q represents the you know this concentration in adsorbent. Now, since adsorbent is the solid phase, this would be, this factor would be multiplied with 1 minus epsilon p. So, I am trying to you know separately write the different terms on the left hand side we have the in minus out sorry the out minus the in. And in that case we write the rate of flux at r plus delta r and the rate of flux at r. On the right hand side, we write the accumulation term of the you know this rate of change of the concentration per unit volume is what is written as the first term where c is the concentration of the adsorbate in the bulk phase.

And, then also we have the term of the adsorbate that is getting adsorbed. So, this is essentially the adsorption term here. So, you can which can be referred to as the appearance or the disappearance term very similar to reaction term. This is the rate of accumulation term right. We also have this on the left hand side the term of mass in and mass out on the left hand side.

So, taking delta r tending to 0 and dividing on both sides by 4 pi you know r 4 pi r delta r 4 pi delta r we can get the equation as 1 by r square del del r of r square d E del C del r is equal to del C del t plus 1 minus epsilon p by epsilon p dq/dt. Now, please remember one particular thing I want to highlight here is the fact that the q here is essentially the bulk averaged quantity that we are talking about or the you know this spatially averaged quantity of the q that is getting absorbed at different you know this location of r. So, of course, q can also be a function of r and t. But generally the rate of diffusion if you are ignoring the rate of diffusion in the solid phase. So, this is what we are considering the diffusion to be primarily important in the solution phase ignoring any diffusion in the solid phase where you will also have the similar flux or the diffusive flux type of equation for diffusion.



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$$= \underbrace{\varepsilon_p 4\pi r^2 \Delta r \frac{\partial c}{\partial t}}_{\text{rate of accumulation}} + \underbrace{(1-\varepsilon_p) 4\pi r^2 \Delta r \frac{\partial \bar{q}}{\partial t}}_{\substack{\text{adsorption kinetic term} \\ \text{(appearance/disappearance)}}}$$

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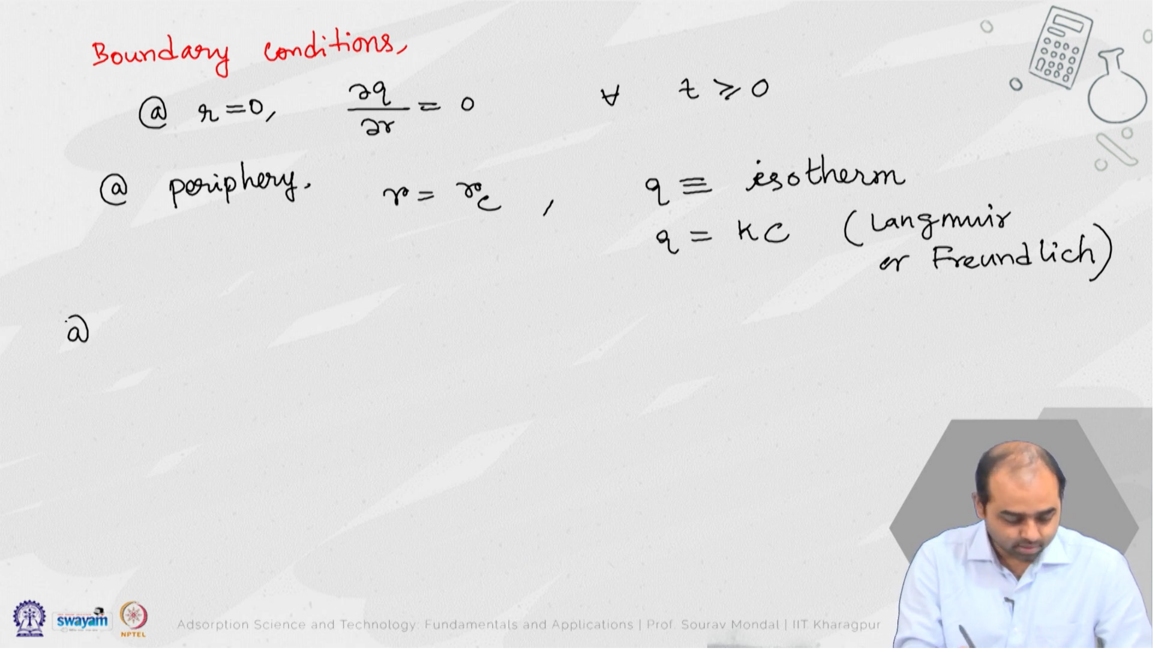
Taking $\Delta r \to 0$

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

Q is being ignored here. So, in that case the diffusion flux that Q is essentially represented already by the equations that we have described where in the first class of this week how the Q is the averaged quantity in the case of you know adsorption within the particle provided the You know the diffusion or whatever adsorption in this sorry the diffusion in this solid particle is comparatively insignificant in this case of diffusion happening simultaneously in the solution phase. So, this is what we try to write down the transport equation in this case having intra particle level of transport in the bulk state or in the solution phase. Now, let us look into the boundary conditions. So, the boundary conditions in this problem is at this is spherical particle at r is equal to 0, we have del q / del r is equal to 0 for all time t greater than 0.



Boundary conditions,

@ $r=0, \quad \frac{\partial q}{\partial r} = 0 \quad \forall \quad t \geq 0$

@ periphery. $r = r_c \,, \quad q \equiv$ isotherm

$q = KC$ (Langmuir or Freundlich)

@

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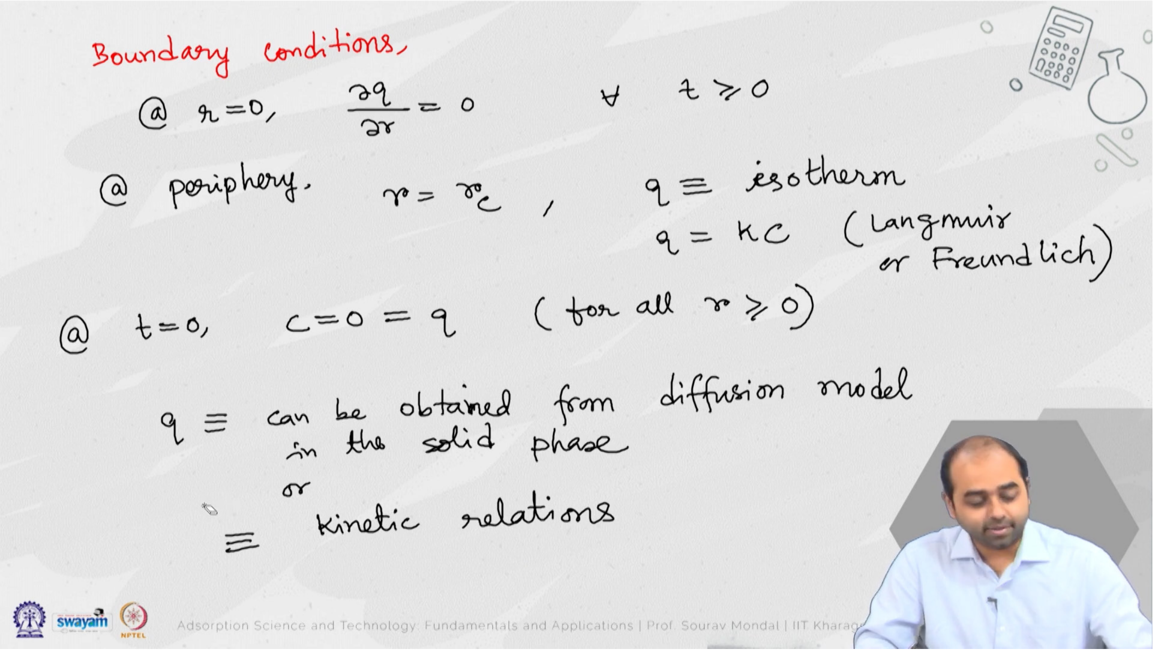
And also at the periphery where is r is equal to r c. Please note that this q follows this isotherm equation because at r is equal to r c the concentration is related to the equilibrium isotherm as it is understood that the particle where the internal transport is very important or the dynamics of the internal in intrinsic transport or the intra particle transport is slow and that is where we are studying the dynamics, it will naturally arrive at an equilibrium value on the surface of the particle or on the surface of the particle. So, this could be defined by simple Henry's law something like k into c or you know the Langmuir type or Freundlich type can also be used in this case. At g is equal to 0, this c is equal to 0 and also q is equal to 0. So, this is the case for all r greater than equal to 0.

Now of course, we are not going to talk about the solution of this system as it is this involves both q and the c. One can also understand that to solve this equation which involves two variables q and the c, the value of dq/dt can be obtained either from the you know this transport equation for the diffusion in the solid phase or one can also. So, this Q can be obtained from diffusion model in the solid phase or it can also be obtained from the kinetic relations. Which is something that we have already discussed in the second week of this course on the different types of the kinetic relations, the pseudo first order, pseudo second order and all of those cases. They can also be used for this part.



Boundary conditions,

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@ $t=0$, $C = 0 = q$ (for all $r \geq 0$)

$q \equiv$ can be obtained from diffusion model in the solid phase

or

$\equiv$ kinetic relations

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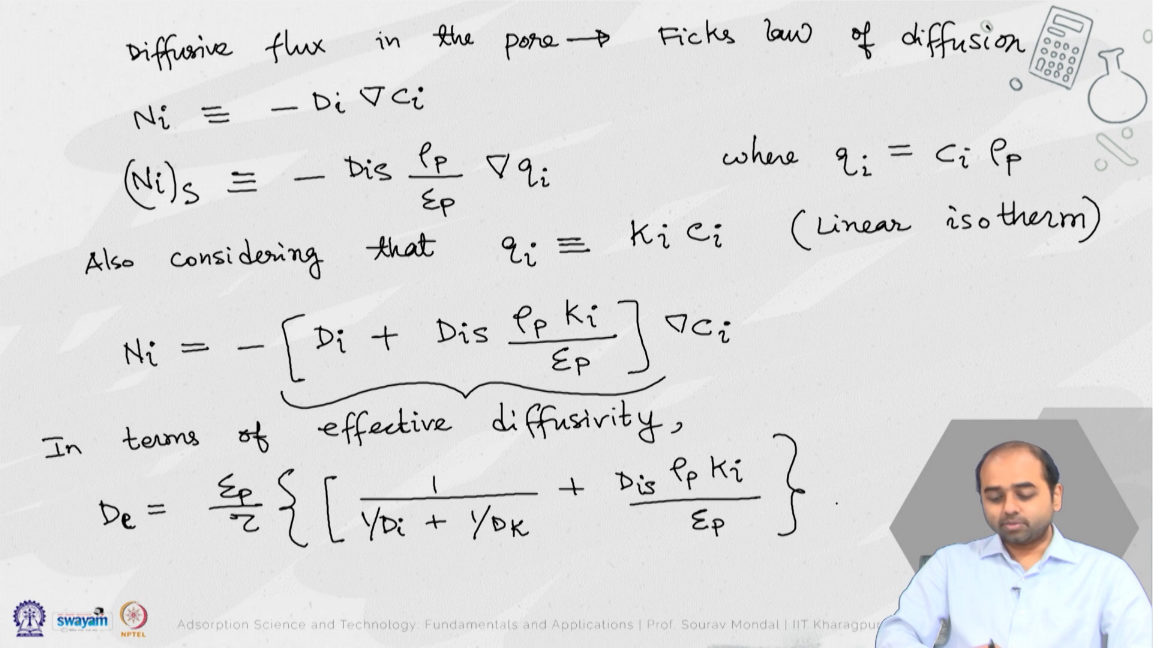
Now, coming to the diffusivities, it is very important to relate the intra particle diffusivity with respect to the bulk diffusivity. So, normally the intra particle diffusivity is represented. So, the diffusive flux in the pore is represented by the Fick's law of diffusion. So this Ni is represented as minus Di grad of Ci. But many a times as you know already we have discussed this in the first lecture that how the diffusivity inside porous material can be related to.

So, many a times and to also convert this you know Ci with respect to the Qi this solid phase flux can be represented as. So, I am intentionally using this subscript S to distinguish it from the bulk phase to the solid phase as something like this where Q sorry. where q i is related to c i into rho p that is multiplied with the particle level density. So, taking this into factor as well as also considering that q can also be related to this ki into ci linear isotherm model. Now, it must be noted that. Fick's law is actually valid for dilute systems and in the dilute concentration range the Langmuir type model very well is related to the linear isotherm model.



Diffusive flux in the pore → Ficks law of diffusion

$$N_i \equiv -D_i \nabla C_i$$

$$(N_i)_S \equiv -D_{is}\frac{\rho_p}{\varepsilon_p}\nabla q_i \qquad \text{where } q_i = C_i \rho_p$$

Also considering that $q_i \equiv K_i C_i$ (Linear isotherm)

$$N_i = -\underbrace{\left[D_i + D_{is}\frac{\rho_p K_i}{\varepsilon_p}\right]}\nabla C_i$$

In terms of effective diffusivity,

$$D_e = \frac{\varepsilon_p}{\tau}\left\{\left[\frac{1}{1/D_i + 1/D_K} + \frac{D_{is}\,\rho_p K_i}{\varepsilon_p}\right.\right\}$$

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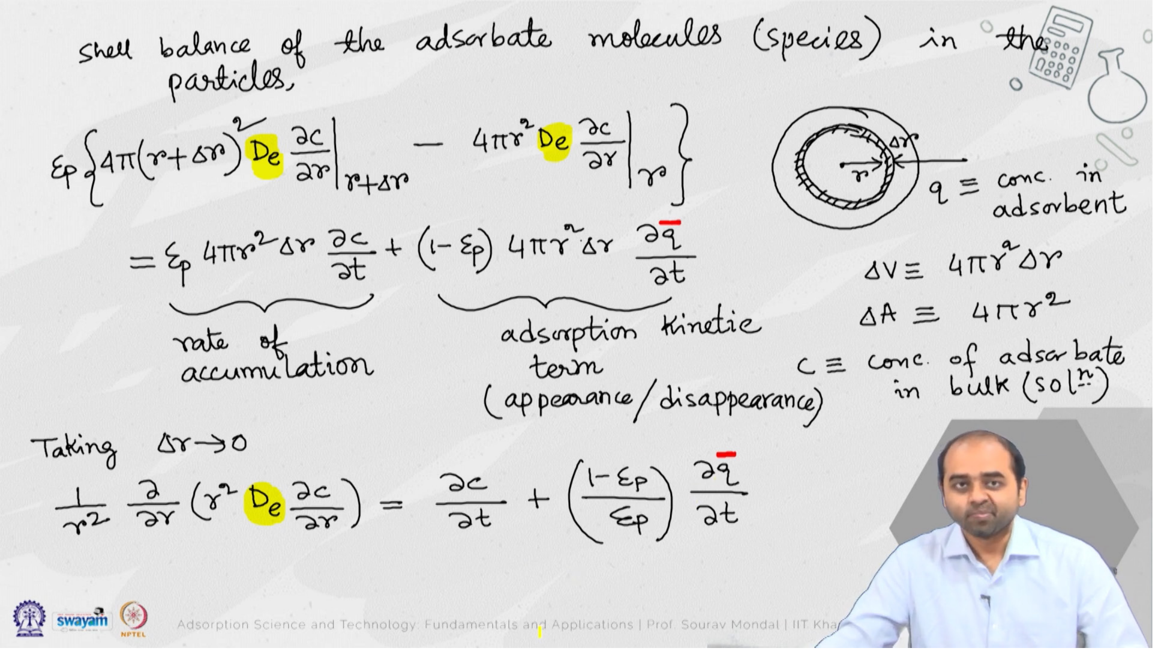
So, in that case one can see that the total you know flux diffusion can be related to the bulk diffusion in the solution phase plus the diffusion in the solid phase as something like this. So, in terms of the, so this is the diffusion coefficient in terms of the effective diffusivity in inter particle transport. where we can bring in the effects of the tortuosity factor and everything the effectivity effective diffusivity is related by this tau into this equivalent you know this phenomena and also if we bring in the this knudsen diffusivity into the picture, one can write a composite expression as something like this. So, please note that this tortuosity factor is for pore volume diffusion and not for surface diffusion. So, this is how the diffusivity in this case of you know intra particle transport or the effective diffusivity that we are referring to in the previous case here is related and this can be computed based on the fact that there is a level of Maxwell type diffusion, Knudsen diffusion, surface diffusion or the solid diffusion as well as diffusion affected due to the porous nature of this material.



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So, this is all about intra particle transport. It we will be talking about you know in the next class related to the slurry mode of the transport or when there is dispersion you know mediated transport or the external transport becomes very important. We will see those models in the next class related to this diffusion in the solution phase. One more thing I want to highlight here that there is a it is very important to understand the relative time scales in the problem. So, there is adsorption time scale, there is this diffusion time scale and there is also the levels of diffusion happening in the solid phase, in the bulk phase within the pore itself.

So, all of these different physics are very important to factor in while trying to simplify your generic system from the purpose of this diffusion coupled with adsorption which is always the case. So, it might also be important to remember when somebody is measuring or when experimentally someone is measuring the equilibrium concentrations, what are the mass transport limiting factors that can seriously affect the intrinsic rate of this adsorption or the adsorption which is actually the true adsorption is often influenced by the level of diffusion happening inside the pores or inside these solid particles. So, these are the different you know physics which is happening at different length scales and time scales that is very important to realize and factor in and accordingly they should be attributed as the dominant or the comparable terms in your overall transport equation. So, with this I close this lecture for today. See you everyone in the next class where we discuss the slurry transport or transport phenomena of adsorption in the solution phase.

So, thank you. Hope all of you like this lecture.