Course: Adsorption Science and Technology: Fundamentals and Applications

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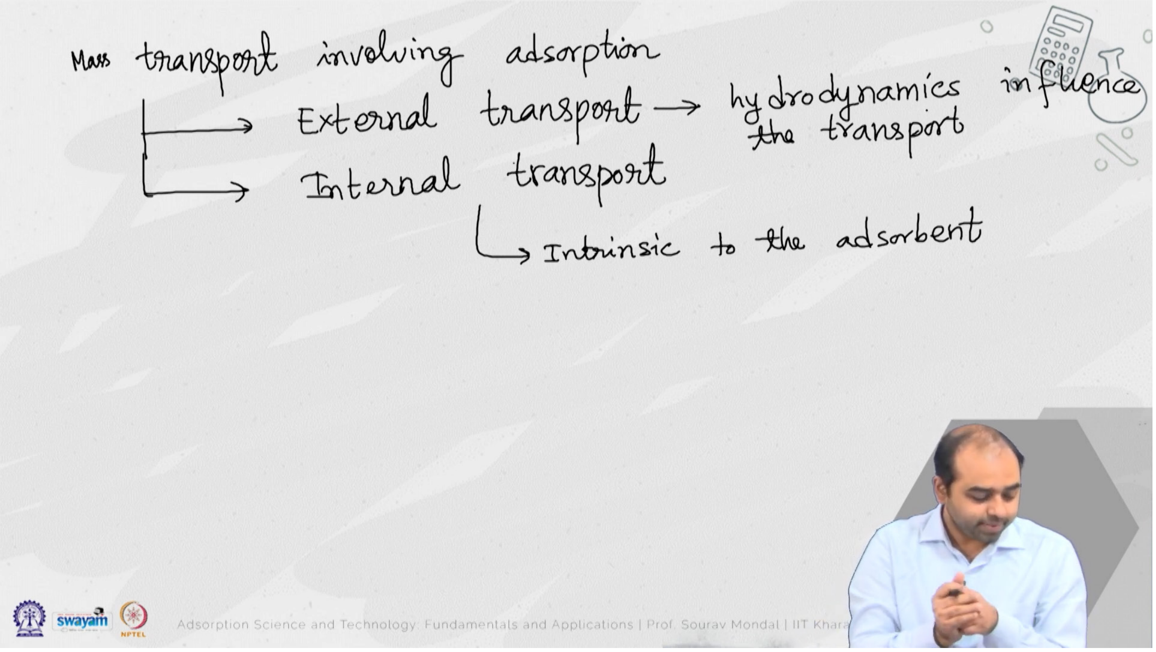
Week 04

Lecture 16 | Adsorption and Diffusion Models

Hello and welcome everyone. In this week we are going to talk about the different kinds of mass transfer you know processes that are often encountered along with adsorption. So, particularly diffusion is a important transport phenomenon which is often associated along with adsorption and many a times it has been observed that the diffusion of the molecules or the adsorbate molecules is a limiting you know step in the process of this overall adsorption. Even though the binding or the attachment or the rate of attachments of the molecules physically to the adsorbent sites is important, the diffusion of these molecules or the time scale of diffusion of these molecules coming in the vicinity of the adsorption sites does play a big role and it is many a times the rate limiting step. Now, to understand the role of diffusion, it is very important to realize that diffusion is actually a process where the molecules move towards the state of low free energy configuration. Now, in the case of adsorption mediated process or adsorption is the dominant role of the process, the diffusion is generally influenced by the nature of the adsorption sites, adsorption characteristics, its porosity, packing, the level of dispersion particularly if it is a packed bed adsorption we are talking about all of these factors.

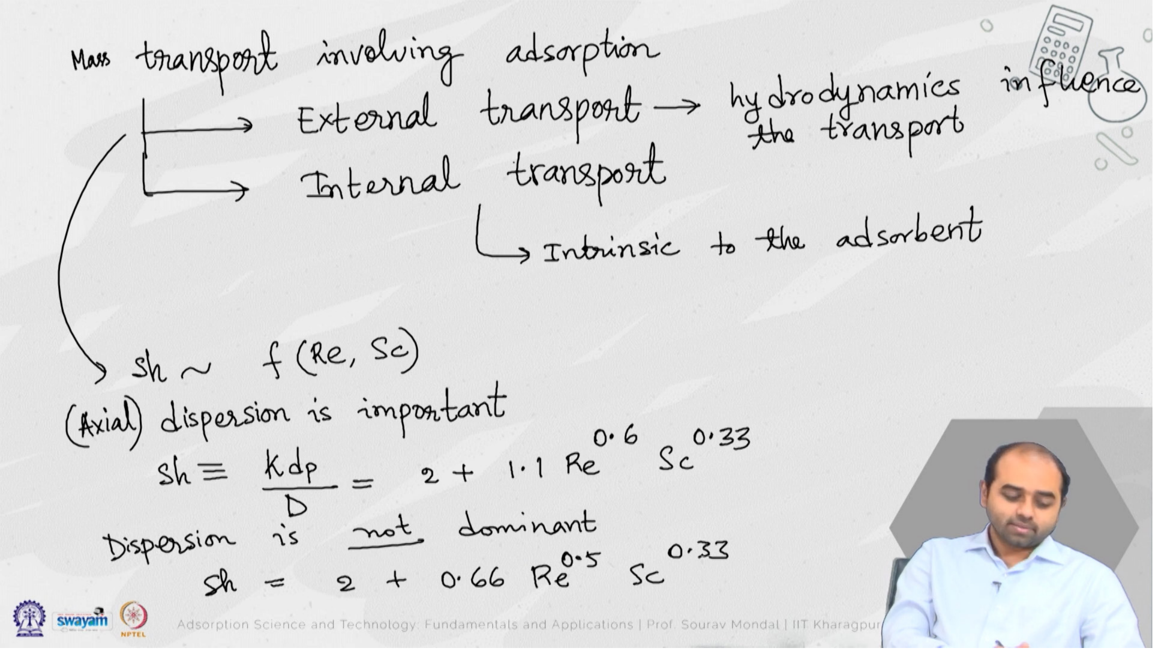


Mass transport involving adsorption

- → External transport → hydrodynamics influence the transport
- → Internal transport
  - → Intrinsic to the adsorbent

So, in this week mostly we will talk about the different types of you know diffusion coupled adsorption models, we will also talk about the film diffusion, we will talk about the linear driving force law, we will talk about intraparticle you know mass transfer, then we will move towards the slurry adsorption where both you know diffusion external transport does play a big role. So, these are the different things that we will be talking about in this week. And, to begin with today's lecture we will be covering some of the introductory you know adsorption diffusion phenomena and how do we explain this diffusion in the context of adsorption. So, typically there are two types of transport phenomena that happens during the process of you know mass transport involving adsorption.

One is external transport and the other is internal transport. So, the external transport can be understood as the transport phenomena that is happening outside of the adsorbent particles or outside of this adsorption sites mostly in the solution phase. And the internal transport is something which is happening intrinsic to the particle or to the adsorbent. So, mostly it is inside the powder structure of the adsorbent where internal transport is happening. So, in the case of the external transport often the mass transfer coefficient it described generally by different kinds of you know Sherwood relationships and that determines that what is the level of you know influence of the hydrodynamics in such cases.



Mass transport involving adsorption

$\longrightarrow$ External transport $\rightarrow$ hydrodynamics influence the transport

$\longrightarrow$ Internal transport

$\hookrightarrow$ Intrinsic to the adsorbent

$Sh \sim f(Re, Sc)$

(Axial) dispersion is important

$$Sh \equiv \frac{Kd_p}{D} = 2 + 1.1\, Re^{0.6}\, Sc^{0.33}$$

Dispersion is not dominant

$$Sh = 2 + 0.66\, Re^{0.5}\, Sc^{0.33}$$

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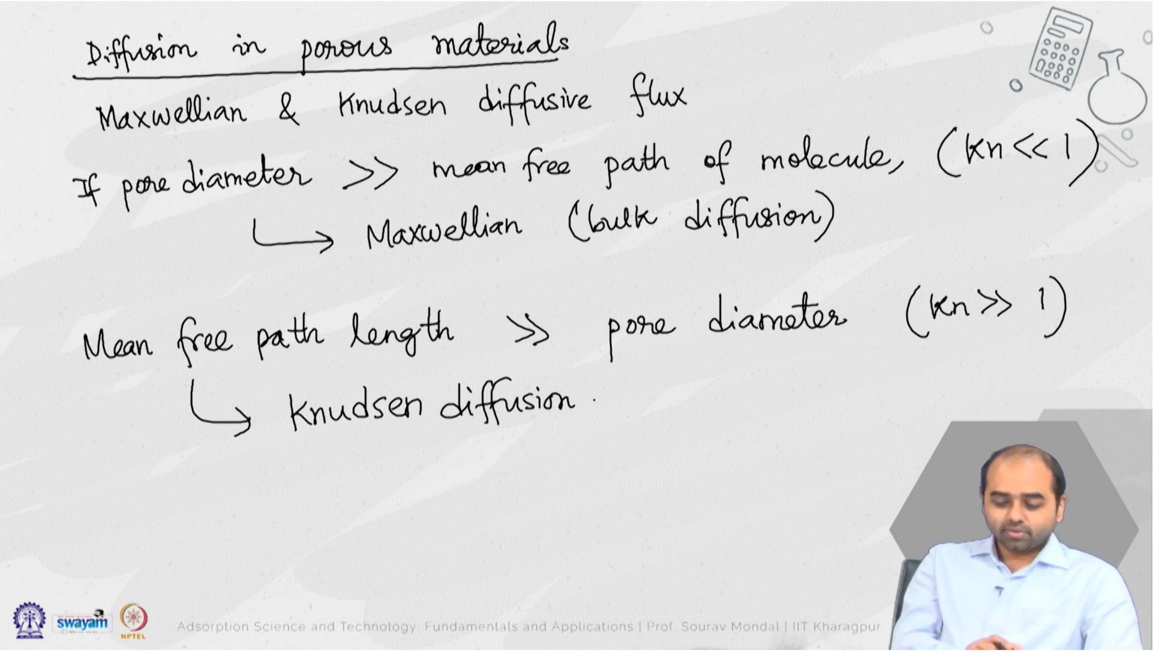
So, in the external transport, hydro dynamics influence the transport. So, typically the external transport case is defined by Sherwood relationships and this is a function of the Reynolds number and the Schmidt number of the system. So, typically for experiments where you know there is a strong influence of the you know axial dispersion. So, if axial dispersion is important, then the Sherwood relation which is the dimensionless form of the mass transfer coefficient k. And generally you define the Sherwood number with respect to considering the characteristic length scale as the particle diameter.

So, this is a Sherwood number relation in the in the level of the particle diameter is equal to 2 plus Reynolds to the power 0.6 Schmidt to the power 0.33. So, typically this is you know the way on how one can quantify the mass transfer coefficient in the case of external transport where axial dispersion is important, particularly when it is not important on when dispersion is not important. Sorry. When dispersion is not dominant then the Sherwood relation is slightly modified as Something like this. And one can understand that this Schmidt number to the power one-third relation is particularly evolved from the fact that the ratio of the mass transfer boundary layer to the hydrodynamic boundary layer scales with Schmidt number to the power half or it is inversely proportional to the you know the cube relation of the diffusivity. So, from this aspect Schmidt number to the power one-third is actually evolved. There is also something based on the Colburn analogy factor which one can also take help of a particularly for situations when Reynolds number is slightly larger or when it is more in the case of porous media transport. The next important is to quantify understand what about the types of diffusion that is happening in porous materials.

It is very important to quantify or to understand the role of or the distinction between the Maxwellian and the Knudsen diffusion coefficients or the Knudsen diffusive flux. So, if the pore, so the way when Maxwell diffusive flux is important or when Knudsen diffusion flux should be considered. So, if the pore diameter is greater than the or much greater than the mean free path of then it is the you know situation with Maxwellian or bulk diffusion model. Whereas, if the mean free path path length is greater than the pore diameter. So, this is the case when Knudsen number is greater than 1 and this is the case when the Knudsen number is less than 1, then this is the situation of the Knudsen you know diffusion dominated transport.



Diffusion in porous materials

Maxwellian & Knudsen diffusive flux

If pore diameter >> mean free path of molecule, $(Kn \ll 1)$

↳ Maxwellian (bulk diffusion)

Mean free path length >> pore diameter $(Kn \gg 1)$

↳ Knudsen diffusion.

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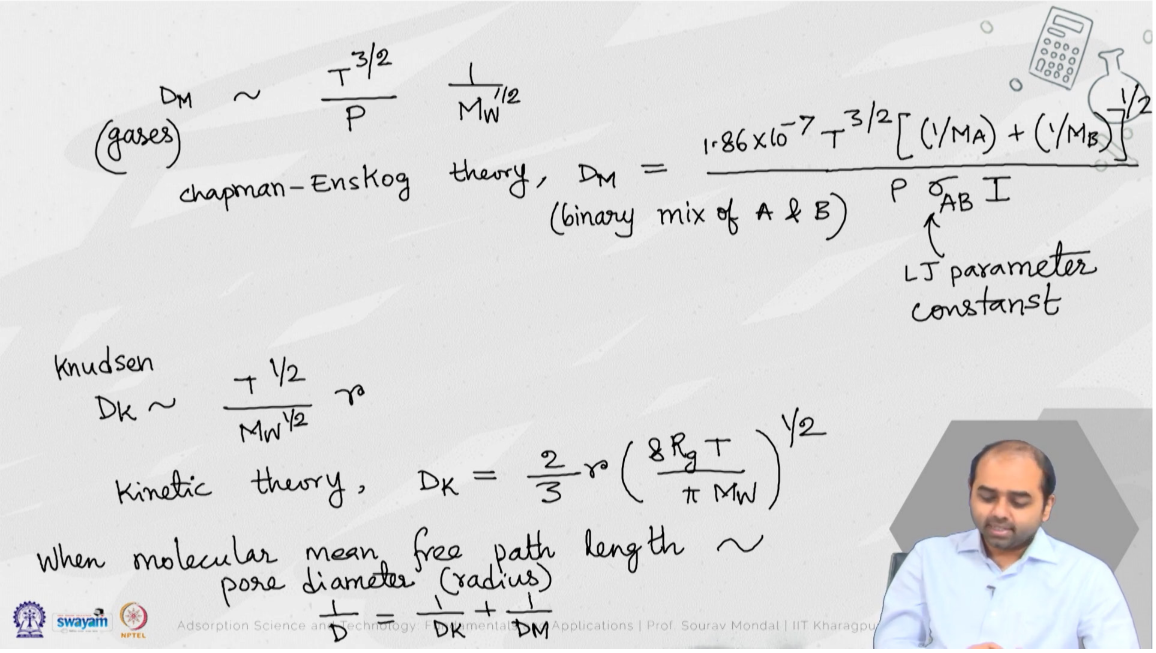
So, both of these you know whether it is the Maxwell type behavior or whether it is Knudsen type behavior, the diffusive flux or the transport flux can be described by means of the Fick's law of the diffusion where the diffusion coefficient is actually different for bulk diffusion and the Knudsen diffusion. So, typically the kinetic theory of the gases reveals that the diffusion of gas is determined from the mean velocity of the molecules right. This is what how originally the diffusivity relations are proposed in terms of the kinetic energy of the molecules or in terms of the overall Brownian motion and the molecular convection. And they tend to you know the distance before they travel before I mean on to collide with each other is generally you know described by this Maxwell type diffusion. But whereas, if they move or get transported or convected, I am talking about about the molecular motion through a narrow path that is where the Knudsen diffusion coefficient or the Knudsen diffusive flux becomes important.

So, typically if the pore diameter is much larger or the characteristic length scale is larger than the mean free path of the molecule essentially the molecular movement is unrestricted or unconstrained and that is what is defined in the bulk diffusion. Whereas, in the case of the Knudsen diffusion it is restricted movement of the molecules and naturally which suggest that the Knudsen diffusion coefficient is highly dependent on the particularly on the you know this pore radius as well as the pore structure characteristics. So, typically the in contrast to a classical you know diffusion coefficient. So, for example, the Maxwell diffusion coefficient is related to the for I mean talking about for gases here particularly for liquids these are slightly different. It is typically proportional to 3 by 2.

It is inversely proportional to the pressure. It is also to some extent dependent on the molecular weight of the molecules. So, this is how the Maxwell relation is dependent on. Typically for the case of you know based on the Chapman and Enskog theory, the Maxwell diffusion coefficient can be for binary systems this is described as through this relation divided by the denominator we have pressure, then there is something known as this Lennard Jones constant for two molecules a and b and a collision integral. So, of course, we are not you know describing too much on these things that is beyond the scope of this current you know syllabus.

So, this is the L J parameter constant. This Lennard Jones potential function description can help us to determine the sigma and I is the collision integral, but whereas for the Knudsen diffusion or the Knudsen diffusivity this is. This is related to of course, with the temperature as half molecular weight, also to the power half and it is proportional to the pore radius or the pore diameter also something we can relate. So, based on this kinetic theory this Knudsen diffusivity can be related to as something like this. Rg is the universal gas constant. So, it is understood that the in the case of when the Knudsen diffusivity is very important, the size of the pore radius does play a big role in determining the rate of the diffusive flux.



(gases) $D_M \sim \frac{T^{3/2}}{P} \frac{1}{M_W^{1/2}}$

chapman-Enskog theory, $D_M = \frac{1.86\times10^{-7}\, T^{3/2}\left[(1/M_A) + (1/M_B)\right]^{1/2}}{P\, \sigma_{AB}\, I}$

(binary mix of A & B)

LJ parameter constanst

Knudsen $D_K \sim \frac{T^{1/2}}{M_W^{1/2}}\, r$

Kinetic theory, $D_K = \frac{2}{3} r \left(\frac{8 R_g T}{\pi M_W}\right)^{1/2}$

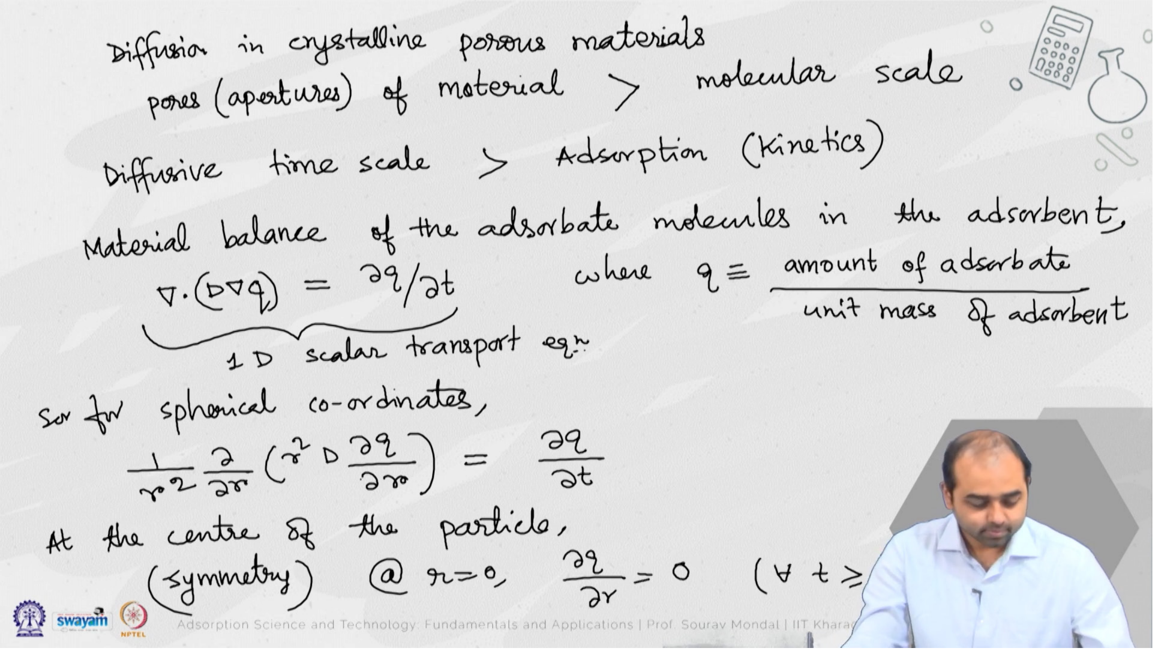
When molecular mean free path length ~ pore diameter (radius)

$\frac{1}{D} = \frac{1}{D_K} + \frac{1}{D_M}$

Particularly when both Knudsen and the you know bulk diffusion is comparable. So, this is the situation when the mean free path length is comparable to the you know this molecular this pore radius of the system. So, when molecular mean free path length is comparable to pore diameter or radius or radius. The overall diffusion coefficient can be related to as the sum of both of these two types of the diffusion coefficient that is the Knudsen diffusion and the Maxwell diffusion coefficient. Now, typically since many a times you know the overall porous nature of the molecule does sorry of the adsorbent.

So, this porous nature of the adsorbent is important and in that case and the adsorbent naturally has a distribution of the pore sizes. So, often it is important or relevant to characterize the diffusion coefficient in terms of the some you know overall property of the porous structure. So, for example, in this case the tortuosity factor is often referred to. And the diffusion coefficient or the effective diffusion coefficient in that case becomes you know a function of the porosity as well as the tortuosity factor. So, typically the tortuosity factor is defined as the ratio of the length of the molecule sorry this path of a particular molecule travelling through a curvilinear approach as compared to a straight approach that is how you know the tortuosity factor is defined in this case.

So, as you can see that always always this porosity is less than 1 and the tortuosity factor is always greater than 1 right, this is the possibility. So, De is always less than the bulk diffusivity or in other words the diffusivity inside porous medium is hindered because of the fact of the porous nature or the porosity of the material. And there are different types of based on the you know this pore size distribution or the effective porosity, there are different formations or different formulations where this relation can be you know more refined or different in other types of situations particularly where the distribution is not unimodal in nature, the pore size distribution is not unimodal in nature. Now, I wanted to talk about the transport equation in the case of where diffusion is particularly important. So, let us think of a you know system of adsorbents which has highly crystalline structure.



Diffusion in crystalline porous materials

pores (apertures) of material > molecular scale

Diffusive time scale > Adsorption (Kinetics)

Material balance of the adsorbate molecules in the adsorbent,

$$\underbrace{\nabla\cdot(D\nabla q) = \partial q/\partial t}_{\text{1 D scalar transport eq}^{n}} \quad \text{where } q \equiv \frac{\text{amount of adsorbate}}{\text{unit mass of adsorbent}}$$

So for spherical co-ordinates,

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D\frac{\partial q}{\partial r}\right) = \frac{\partial q}{\partial t}$$

At the centre of the particle,

(symmetry) @ $r=0$, $\frac{\partial q}{\partial r} = 0$ $(\forall\ t \geq$

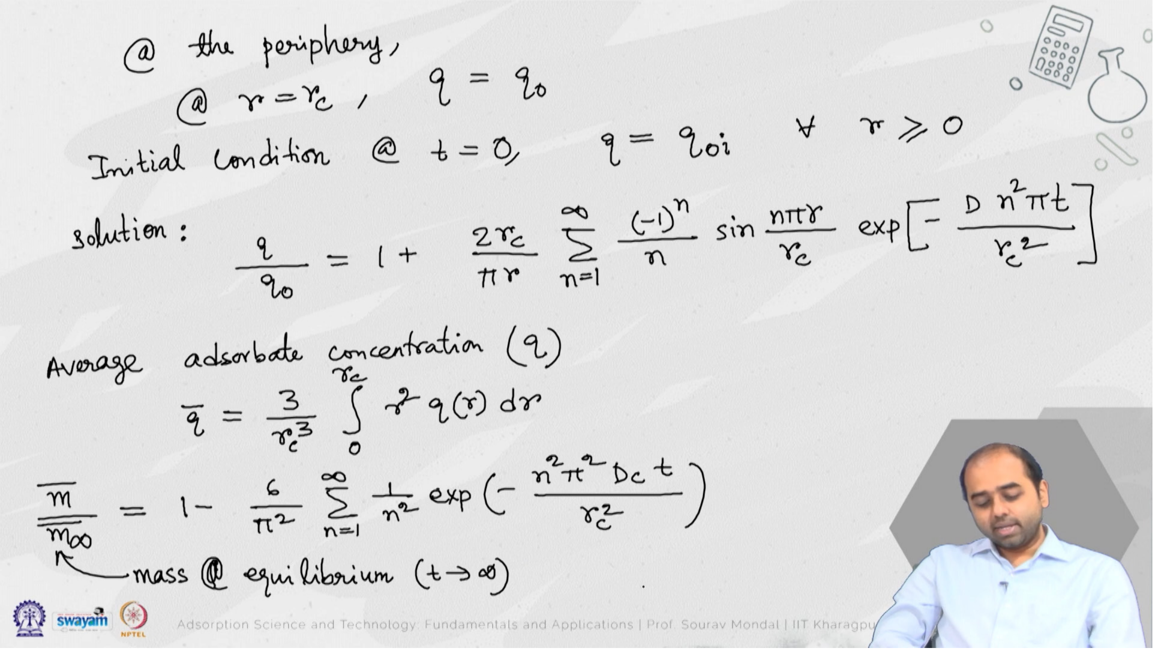
So, for example, you know diffusion if we talk about diffusion in crystalline porous material. So, where the pores or the apertures of the material or the crystalline structure is larger than the molecular scale of the movement. In this case typically the although the diffusivity is not of the Knudsen type because the pores are larger than the molecular scale. But essentially the because of the you know this porosity of the material the diffusion would be slow and so essentially the diffusion would be the controlling factor in the case of the dynamics of the system. So, the diffusive time scale is larger than adsorption, essentially the kinetics becomes important in this scenario.

So, this is the you know possibility which does exist in the case of where this diffusion or the diffusion time scale is actually the slowest step. So, in this case from a you know this material balance diffusion sorry material balance of the adsorbate of the adsorbate molecules in the adsorbent in the adsorbent can be written down by the classical you know this species transport sorry. as something like this where. So, this is the classical you know 1D scalar transport equation and in this case we write the transport equation for the adsorbate phase in the adsorbent. So, where Q is the amount of adsorbate per unit mass of adsorbent.

So, for spherical coordinates. So, assuming we are dealing with spherical you know this adsorbate adsorbent particles and for constant diffusivity this d one can write this as something like this. So, we are considering the Fick's law of diffusion, or the adsorbate species inside the particle. So, at the center of the crystal or the center of the particle will be having the symmetry condition. So, at r is equal to 0, dq/dr is equal to 0 of course, for all time.

At the periphery or on the surface of this crystal, so that is at r is equal to the size of the particle, this would be a Dirichlet condition and initial condition suggest that at t is equal to 0, again this would be equal to something of a different value for all r greater than 0. Now, this is a this is a one dimensional parabolic PDE with suitable transformation one can solve this equation using separation of variables technique. And on solving this equation the equation that you get takes this form. So, this is solved using the method of separation of variables you define two auxiliary equations and then you apply the boundary conditions on there, then you apply finally, the this condition of the orthogonality for the trigonometric function and this is something you will be getting in that case. Now the important is the average adsorbate concentration.

Average adsorbate concentration or the value of q which can be computed from the fact that you do a, you know this spherical average of this concentration. So, this is nothing but based on the fact that we do a average concentration and then integrate it over the you know this volume. So, this is how this average concentration would be looking like. So, typically if you want to consider or work out the mass of the or the mass fraction approach towards equilibrium or towards the equilibrium value which is the situation when t reaches to infinity. So, we define we can define one can define as something like.



@ the periphery,

@ $r = r_c$, $q = q_0$

Initial condition @ $t = 0$, $q = q_{0i}$ $\forall$ $r \geq 0$

solution :

$$\frac{q}{q_0} = 1 + \frac{2r_c}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r}{r_c} \exp\left[-\frac{D n^2 \pi t}{r_c^2}\right]$$

Average adsorbate concentration (q)

$$\bar{q} = \frac{3}{r_c^3} \int_0^{r_c} r^2 q(r)\, dr$$

$$\frac{\overline{m}}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_c t}{r_c^2}\right)$$

mass @ equilibrium $(t \to \infty)$

So, this is the situation which you get as you know this mass fraction or this mass at equilibrium, that is t tending to infinity. So, this ratio, so we are doing this the average quantity will take this form. So, we are doing this fractional average for this system with respect to the equilibrium concentration. So, this will give us the dynamics of the system which is limited by diffusion that how the concentration profile looks in this case when in terms of the equilibrium value with respect to time for you know diffusion limited process. So, I think this gives us some fair idea about how diffusion can be relevant in problems particularly involving adsorption simultaneously.

So, I think all of you have got some fair understanding about the role of diffusion in the mass transport due to adsorption. So, thank you. See you all in the next class.