Course: Adsorption Science and Technology: Fundamentals and Applications

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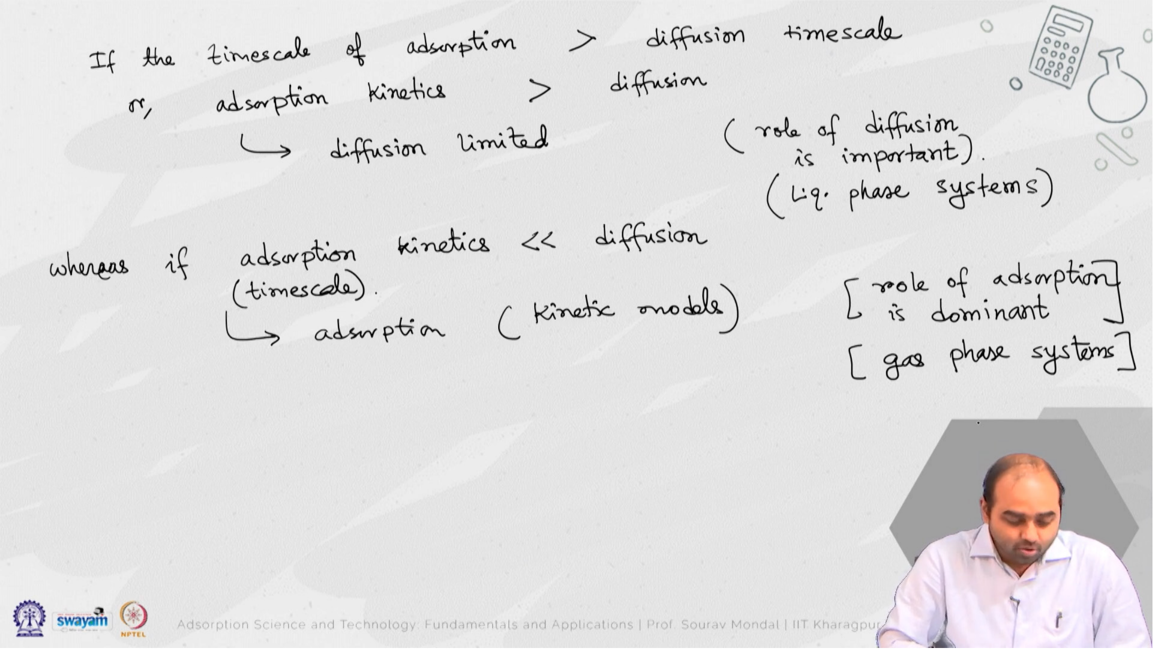
Week 04

Lecture 18 | Linear Driving Force Model

Hello everyone, welcome to this you know third week sorry fourth week of the lecture and in this week we are as you know we are discussing about the different diffusion influenced you know adsorption based separation processes. In the last class we have talked about the role of the film diffusion particularly the different types of diffusion which is happening and when film diffusion is important and how the mass transport equations can be evolved for different scenarios. So, in this class we are going to talk about particularly on the linear driving force relation and this is important to you know convert the system into lumped parameter systems or homogeneous diffusion model. So, particularly the you know this interpretation of the kinetic information or the adsorption kinetics, could be due to the effect of the adsorption or the adsorption time scale. It could be also because of the you know diffusion or the diffusion time scale. So, whichever is the slower step will actually govern the process particularly for gas adsorption as you know the diffusivity is fast or the time scale of diffusion is small.

In that case it is primarily you know determined the adsorption kinetics is primarily defined by the kinetic theories which are some of the types related to zeroth order, first order or pseudo first order and pseudo second order models. But whereas in the case of mass transfer limited particularly diffusion limited process in liquid systems this kinetic theory the kinetics is much faster compared to the scale time scale of the diffusion. So, it is under that scenario the adsorption kinetics needs to be modified or you know suitably accounted for with this diffusion. So, if the time scale of adsorption is greater than diffusion time scale or adsorption kinetics is faster than then the process is diffusion limited.

And in that case this you know role of diffusion is important. And this is particularly true for liquid phase systems. I mean this cannot be treated as like a that all liquid phase systems does follow this, but mostly for liquid phase systems this is true. As diffusivity in liquid phase systems is diffusivity of the adsorbate species is you know lower or smaller compared to diffusion in gas phase systems. If adsorption kinetics is slower than diffusion or the time scale of adsorption is slower than diffusion, then in that case the process is limited by adsorption.



If the timescale of adsorption > diffusion timescale

or, adsorption kinetics > diffusion

↳ diffusion limited (role of diffusion is important).

(Liq. phase systems)

whereas if adsorption kinetics << diffusion (timescale).

↳ adsorption (kinetic models) [role of adsorption is dominant]

[gas phase systems]

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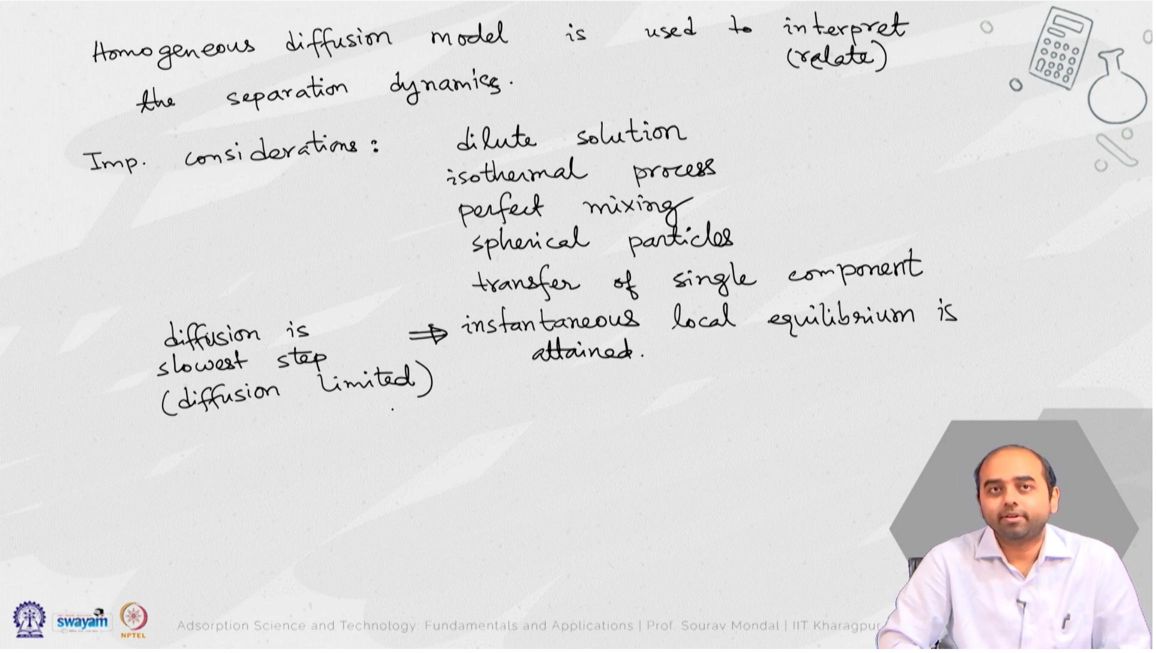
And in that case you need to use the kinetic models and this is particularly true mostly for gas phase systems, but I would also like to apprise here that there are scenarios when even in gas phase it is limited by diffusion and even in liquid phase it is limited by adsorption. So, the other way round scenarios are highly possible. Because diffusion inside packed beds or inside porous mediums is generally also affected by the level of porosity as well as the particle size and whatever this packings that is present. So, the level of porosity also hinders the diffusion coefficient or the diffusion rate. And it may happen that the adsorption kinetics is smaller than the or slower compared to the diffusion time scales in that case even for you know liquid phase systems this may be true.

So that is you know sorry for gas phase systems that may be true. So there are scenarios where in gas phase systems also it could be limited by diffusion that is what I am try to mean here. So, the homogeneous you know diffusion model is generally used to interpret or to relate I would say interpret or relate the separation dynamics. And the important considerations here are dilute solution which necessarily implies fixed law can be applicable in this scenarios. Isothermal process of course perfect mixing there is no heterogeneity or non-uniformity of the process spherical particles transfer of single component.



Homogeneous diffusion model is used to interpret (relate) the separation dynamics.

Imp. considerations : dilute solution
isothermal process
perfect mixing
spherical particles
transfer of single component

diffusion is slowest step (diffusion limited) ⇒ instantaneous local equilibrium is attained.

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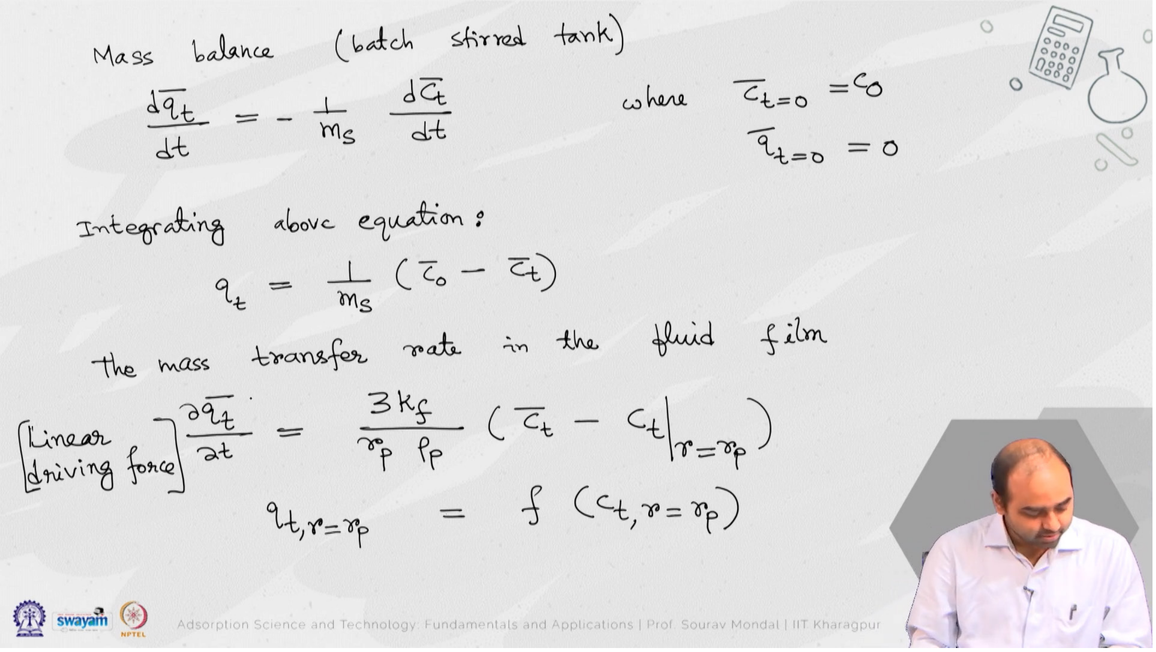
Of course, this can be extended to multi components. Then another important is that instantaneous in a local equilibrium is attained. So, this last condition tells us that diffusion is slowest step as this process is limited by diffusion. Since we are considering that instantaneous local equilibrium or this you know adsorption is like instantaneous in nature or it is very fast. And that is the scenario when the kinetics are generally ignored and you model the dynamic phenomena with the diffusion behaviour or diffusion limited or mass transfer limited step.

So, from a simple mass balance, from a simple mass balance in a batch stirred tank setup, you can write the rate of adsorption as a function of the concentration change with respect to time, where C at t is equal to 0 is 0 or C0 initial concentration but q at t is equal to 0 is actually 0. So we write everything in terms of bar to represent these are like averaged quantities or bulk averaged quantities. Now it must be understood or I want to emphasize that concentration of the adsorbate in the solid is used for adsorbed or immobilized species and here it should not be confused with the free species concentration inside the pores of the solid phase. So, integrating this equation you can get this and of course the mass transfer rate in the fluid film is already represented by this form. This is something which we have already you know explained or discussed in the previous class where this is at the exit of the pore.



Mass balance (batch stirred tank)

$$\frac{d\bar{q}_t}{dt} = -\frac{1}{m_s}\frac{d\bar{C}_t}{dt}$$

where $\bar{C}_{t=0} = C_0$

$\bar{q}_{t=0} = 0$

Integrating above equation:

$$q_t = \frac{1}{m_s}\left(\bar{C}_0 - \bar{C}_t\right)$$

the mass transfer rate in the fluid film

[Linear driving force] $$\frac{\partial \bar{q}_t}{\partial t} = \frac{3k_f}{r_p\,\rho_p}\left(\bar{C}_t - C_t\big|_{r=r_p}\right)$$

$$q_{t,r=r_p} = f\left(C_{t,r=r_p}\right)$$

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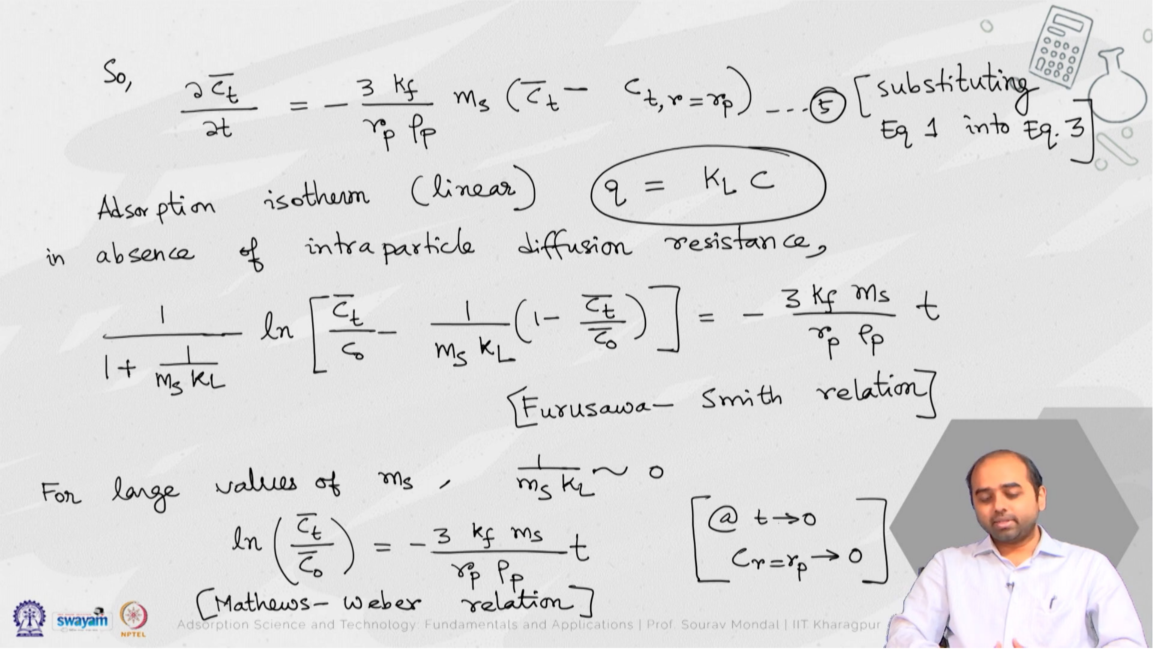
So if you recall this is the lumped parameter model and where it is limited by the you know diffusion this is something we write in the case of diffusion limited process that the driving force in this scenario is the difference in the concentration from the bulk with respect to the surface of the particles and kf is the mass transfer coefficients and this is what is related to the rate of change of the solid phase adsorbate concentration. So, this is essentially the linear driving force equation. So it may be noted that q at any time t at the surface of the pore is in equilibrium the concentration at the surface of the pore because we assume that there is instantaneous. So, this is in the subscript because it is assumed that there is instantaneous equilibrium which is achieved between the adsorbate species and the solid phase concentration. So, now this you know this if this is achieved then this previous equation which I have written down in case of the mass transport rate in the fluid film can be can be substituted means from q to C with some function that is the mass of the solid adsorbent.

So, you can write down dC of dt as like minus 3kf by rho p. So this is possible because this is something we are substituting from this expression itself. Let us call this as expression 1. This is expression 2, 3, 4. So I am trying to substitute equation 1 into equation 3.

So this we get by substituting equation 1 into equation 3. Now here we can use the adsorption isotherm relation. So for example if one considers a linear adsorption isotherm model where q is equal to kL into C typical Henry's law type adsorption and in the absence of intra particle diffusion resistance the above equation can be solved and one can get an expression of this model equation. So, this model equation let me write it down the expression. This is the equilibrium relation kL is the equilibrium constant.

This is known as the Furusawa-Smith relation. This is applicable for the case of linear driving force model for other driving types of driving force this may not you may not arrive at a analytical solution but this is can be related that for linear isotherm the equation or this you know linear driving force equation can be resolved. Now there are some simplifications. For example, I mean here we have assumed that there is linear relation and the linear relation isotherm can also be represented with respect to Q0 by C0 etc. That for large values of ms, one can assume that ms into kL is equal to 0.



So,

$$\frac{\partial \bar{C}_t}{\partial t} = -\frac{3 K_f}{r_p \rho_p} m_s \left(\bar{C}_t - C_{t, r=r_p}\right) \quad \text{---} ⑤ \quad \left[\text{substituting Eq 1 into Eq. 3}\right]$$

Adsorption isotherm (linear) $\boxed{q = K_L C}$

in absence of intraparticle diffusion resistance,

$$\frac{1}{1 + \frac{1}{m_s K_L}} \ln\left[\frac{\bar{C}_t}{C_0} - \frac{1}{m_s K_L}\left(1 - \frac{\bar{C}_t}{C_0}\right)\right] = -\frac{3 K_f m_s}{r_p \rho_p} t$$

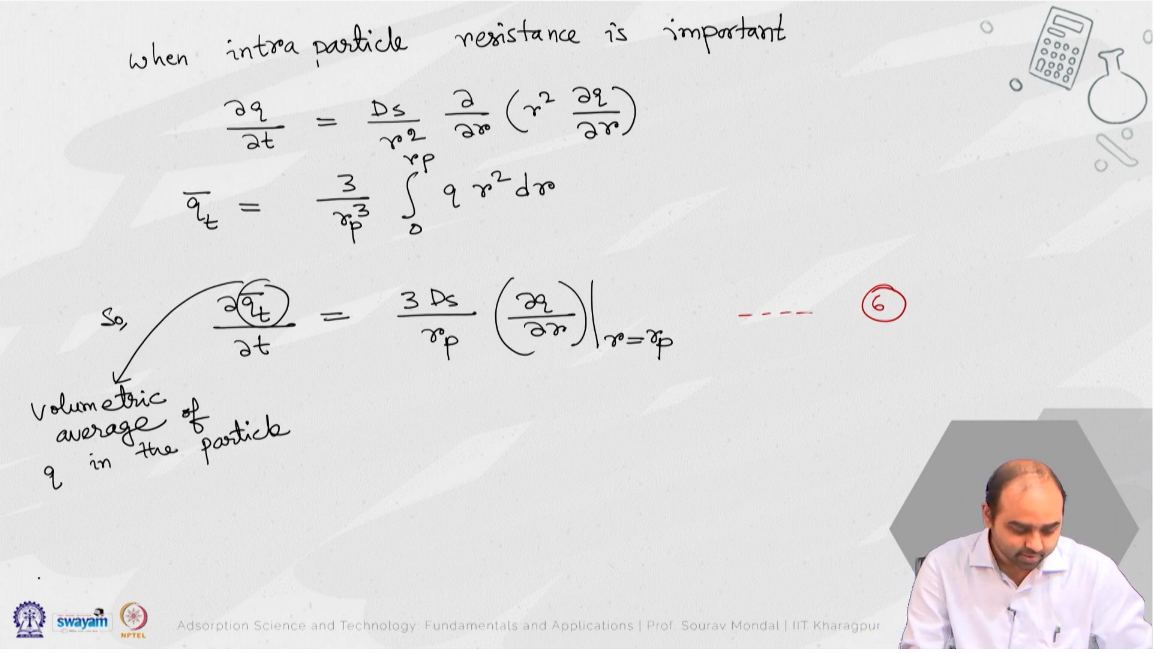
[Furusawa– Smith relation]

For large values of m_s, $\frac{1}{m_s K_L} \sim 0$

$$\ln\left(\frac{\bar{C}_t}{\bar{C}_0}\right) = -\frac{3 k_f m_s}{r_p \rho_p} t \qquad \left[\begin{array}{l} @\ t \to 0 \\ C_{r=r_p} \to 0 \end{array}\right]$$

[Mathews– Weber relation]

In that scenario this expression gets simplified to something like this. something like this. So, this can also be derived I mean this instead of this approximation of you know ms being very large if you also say that at you know at t is equal to 0. This c of r is equal to r p is equal to 0 if this is something also set in this equation this let us call this as 5 in this equation if that is set then you can also derive or arrive at this that this equation which is generally referred to as the mathews-weber relation and this is particularly true for large values of ms in this case so particularly for large mass of the particles or the particle size to be quite large the surface concentration may actually be close to zero or instead the equilibrium isotherm constants can sorry the equilibrium that is achieved can also greatly reduce the concentration on the surface of the pores. And in that scenario the concentration in the you know liquid phase or in the bulk phase outside the particles can follow an exponential relation.



when intra particle resistance is important

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

$$\bar{q}_t = \frac{3}{r_p^3}\int_0^{r_p} q\, r^2\, dr$$

So,

$$\frac{\partial \bar{q}_t}{\partial t} = \frac{3 D_s}{r_p}\left(\frac{\partial q}{\partial r}\right)\Big|_{r=r_p} \quad ----\ \text{⑥}$$

volumetric average of q in the particle

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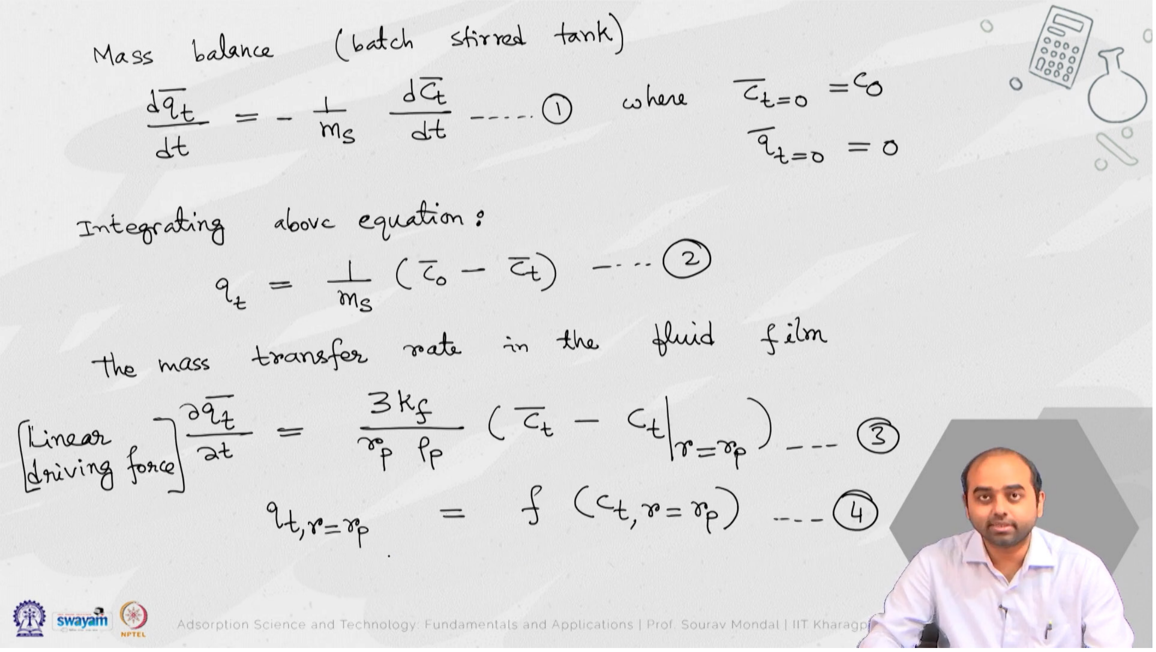

Mass balance (batch stirred tank)

$$\frac{d\bar{q}_t}{dt} = -\frac{1}{m_s}\frac{d\bar{C}_t}{dt} \quad ----\ \text{①}$$

where $\bar{C}_{t=0} = C_0$

$\bar{q}_{t=0} = 0$

Integrating above equation:

$$q_t = \frac{1}{m_s}\left(\bar{C}_0 - \bar{C}_t\right) \quad ----\ \text{②}$$

The mass transfer rate in the fluid film

[Linear driving force]

$$\frac{\partial \bar{q}_t}{\partial t} = \frac{3 k_f}{r_p\, \rho_p}\left(\bar{C}_t - C_t\Big|_{r=r_p}\right) \quad ---\ \text{③}$$

$$q_{t,r=r_p} = f\left(C_{t,r=r_p}\right) \quad ---\ \text{④}$$

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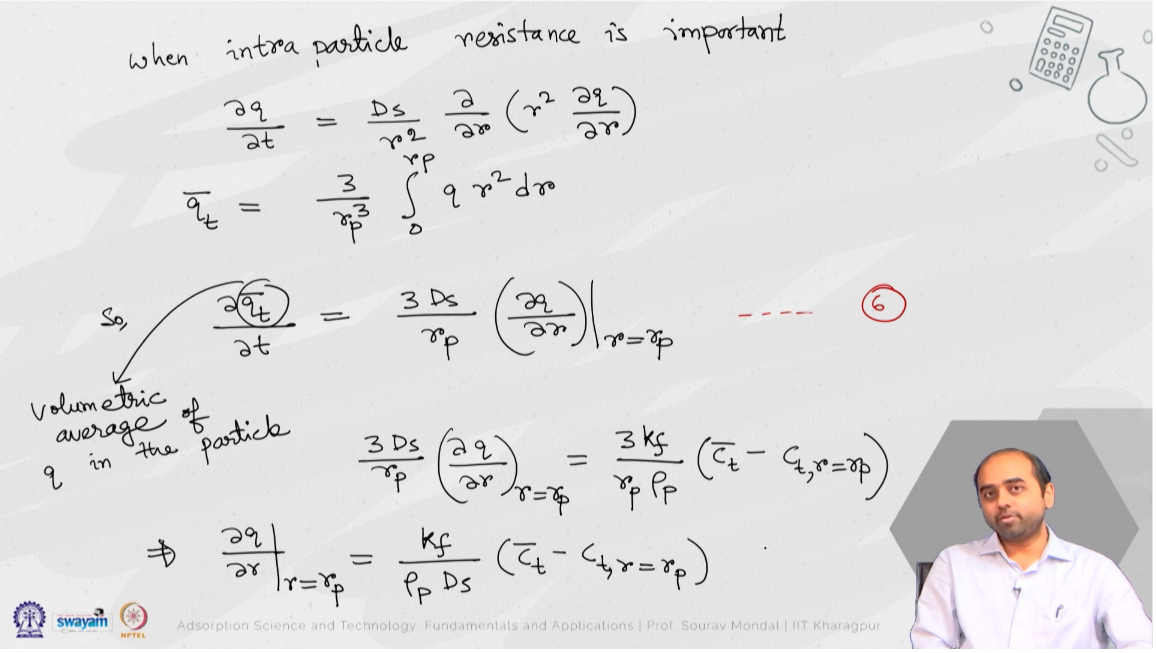
In the case of when the intraparticle resistance becomes important of course that is something we have already talked about in the beginning of this week. In that scenario, of course, the concentration in the solid phase, the surface diffusion also follows the Fick's law and the unsteady equation can be written down something like this. And the relationship between average and local concentration can be represented by the you know this integration or the volume averaged integration. So, using this relation one can obtain the average and you know this dynamic term or the average qt is the volumetric of q in the particle can be represented as in terms of the overall material balance at r is equal to rp. Now to solve this equation of course the symmetry condition etc., can be utilized. Now important to note that if this is related then from the previous relation of this equation 5 or particularly when we say that there is instantaneous in equation 3 in equation 3 where we say that there is instantaneous you know this equilibrium. So, Qt can be replaced by Ct etc. Now, in terms of Qt this expression can be used let us call this expression as equation 6. This can be used in relation 3 here and one can get the relation where intraparticle diffusion is important as something like this. Now, of course, here we can you know do some algebraic simplifications and this and be written down as.

So, this is the scenario that when the solid and the fluid phase mass transfer resistance are present the two mass transfer rates are actually equal at the solid surface and we suggest that there is no accumulation of the solid surface. This is the kind of equivalent driving force relation or the mass transport relation that one can you know achieve or one can arrive at. So, this entire exercise we tried to see or we tried to explain the different you know relations you know arriving from the linear driving force law particularly in the scenarios of diffusion limited process whether it is surface diffusion whether it is film diffusion whether it is intra particle or outside of the particle. But in all of this diffusion limits the process and in that case the kinetics is actually ignored and this is particularly true in the case of liquid phase mass transfer system. So, with this I would like to close the lecture today.



when intra particle resistance is important

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

$$\bar{q}_t = \frac{3}{r_p^3}\int_0^{r_p} q\, r^2\, dr$$

So,

$$\frac{\partial \bar{q}_t}{\partial t} = \frac{3D_s}{r_p}\left(\frac{\partial q}{\partial r}\right)\Bigg|_{r=r_p} \quad ---- \quad \textcircled{6}$$

volumetric average of q in the particle

$$\frac{3D_s}{r_p}\left(\frac{\partial q}{\partial r}\right)_{r=r_p} = \frac{3k_f}{r_p\rho_p}\left(\bar{C}_t - C_{t,r=r_p}\right)$$

$$\Rightarrow \frac{\partial q}{\partial r}\Bigg|_{r=r_p} = \frac{k_f}{\rho_p D_s}\left(\bar{C}_t - C_{t,r=r_p}\right)$$

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I hope all of you found it useful and you have realized that in the estimation of the liquid and the solid phase mass transport coefficients whether it is the adsorption coefficients or the adsorption constants or whether it is the constants present in the diffusion or the diffusivities it is important to factor in the you know the relative importance between the two types of separation driving forces that is present here particularly from the liquid phase as well as from the solid phase. So, thank you everyone. See you in the next class where we talk about more on intraparticle transport and we see the different types of diffusivities that is playing a role in that scenario. Thank you.