Microscale Transport Processes

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Lecture No. # 17

Dispersion (Contd.)

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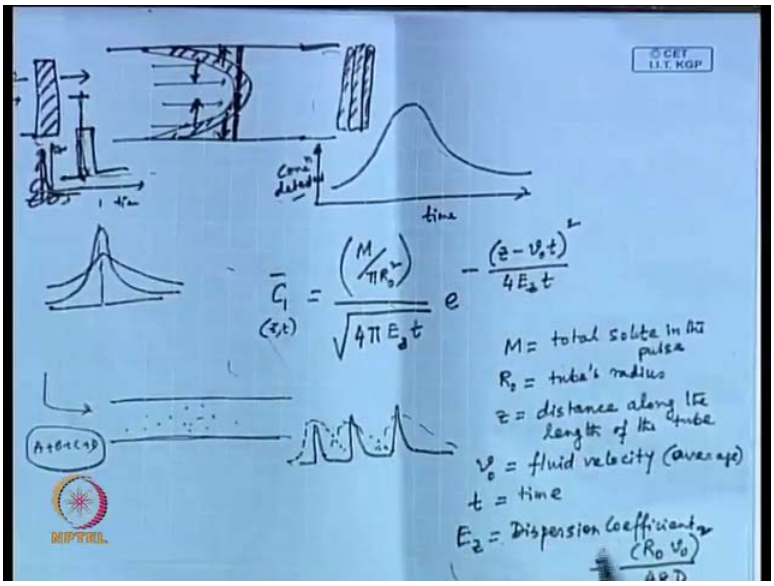

$$\bar{C}_{1(z,t)} = \frac{\left(M/\pi R_0^2\right)}{\sqrt{4\pi E_z t}}\, e^{-\frac{(z-v_0 t)^2}{4E_z t}}$$

M = total solute in the pulse

R_0 = tube's radius

z = distance along the length of the tube

v_0 = fluid velocity (average)

t = time

E_z = Dispersion coefficient $\frac{(R_0 v_0)^2}{48D}$

I welcome you to this class of micro scaletransport process, what we have been discussing is dispersion more importantly the Taylor dispersion.The dispersion that we have been talking about iswhat we have done in the last class.We have discussed aboutslug oror pulse that is going into the tube, which isthrough which the laminar flow is taking place; that means, there is a parabolic velocity distribution already developed and you are introducing a small slug.

So, what we studied at that time is the deformation of the slug,because of this parabolic velocity distribution,because the center central portion of the tube would be flowing faster, that will have a higher velocity, whereas the one the layer that is adjacentto the wall, that would bemoving at a slower rate ornext to the wall it would beat the wall the velocity is 0. So, you have the flow taking place in a parabolic manner.So,that there would be this slug would be deformed.So, that is the hashed portion that we have discussed in the last class.

So, this slug will be deformed. So, when you collect this at the outlet; mind it that this dimension is very small here, and this is this type of dispersion is important, when the dimension is small actually. So, what you collect at the outlet is basically theif if you collect them layer by layer; that means, what you collect is the average over the entire cross section,and then the next block that arise then the next block that arise and if you find theifyoufind theaverage concentration of this layer.

Then the next one that arise, the average concentration that means, at any point you are you are finding the average over the entire cross section.So, some part would be higher concentration of solute because of this deformedpulse and and the other part will have no solute.Because the there wasnot any solute this layer is moving at a slower rate. So, if you plot the concentration at the detector.Detector means, the concentrationaverage concentration of this block that is detected by the detector which is positioned at the outlet.There if you find if you plot the concentration detected as a function of time, what you see is a distribution,because the first layer will have some concentration then there would be some concentration, then there would be some other concentration what what ideally you would expected is that you have introduced a pulse.Pulse is like this or if you are if you are looking at a Diracfunction type pulse then it would be practically high value atat0 and then rest of the places it is all 0.

So, this is this is the type of pulse you are looking at, but at the outlet you are seeinga pulse, which is which has a distribution.And this is what we are referring asTaylor dispersion.And we at the very outset I said that this concentration thethe ififsomebody tries totries to plot, tries to express this C 1 bar. C 1 bar is the average concentration over this entire cross section, for a particular layer that as a function of z and t. What does this mean? Z is the length of the length after which you are collecting itand t is the time.

So, so, as a function of z and t, you would be getting this concentration, this thisyou have a this kind you have a this kind of functionality.And IItold you at that time that this functionality has somesomething in common to what we have already discussed before. When we talked aboutwhen we talked about diffusion of a spot of tracerin an infinite medium, we had a very similar expression that time. However, there instead of E z,we had that diffusivity term and instead of z minus V 0 t, I think we have justwe have some dimensional length there. Here, this z minus V 0 t is I mean it is it must be obvious to you that you are trying to put together a moving coordinate system. V naught t is that distance that the that the pulse would have moved at an average velocity V 0 in time t.

So, this z minus V 0 t isan off shoot ofgoing to a moving coordinate system and this E z is equivalent to diffusivity.Now,we are we are trying to write down at least the governing equations that leads to these equationtheseleads to this expression. However, I would likeand I have already pointed out to you that this E z,which is which we are referring as dispersion coefficient,which is the term equivalent to diffusion coefficientin case of a diffusion of a spot of dye in an infinite medium.

Now, this E z this time we are calling, it a dispersion coefficient and the expression for this dispersion coefficient.Here, I see the D;the diffusion coefficient or diffusivity that is appearing in the denominator, on the other hand in the numerator you have R 0 V 0. So, this isthis thisdependence is completely I mean ititinversely depends on D; where as you expected this to be equivalent to the diffusivity term,if it is equivalent to the diffusivity term then D should have been in the numerator, but instead of that D has gone to the denominator. So, that is thethat is the interesting part of it.

So, what this means is, if something has a higher diffusivity, if something diffuses very fast in the liquid, then you expected that then then probably that it spreading would be more, but in case of aTaylor dispersion the spreading would be less in that case.On the other hand, if something is flowing at a highvelocity that can contribute in a major way to the tothe dispersion. So, this is this is what I what I have given you at that time, and then what I have done is I have I have written down I mean, I have tried to put down these governing equation you pick we pick up a differential element.

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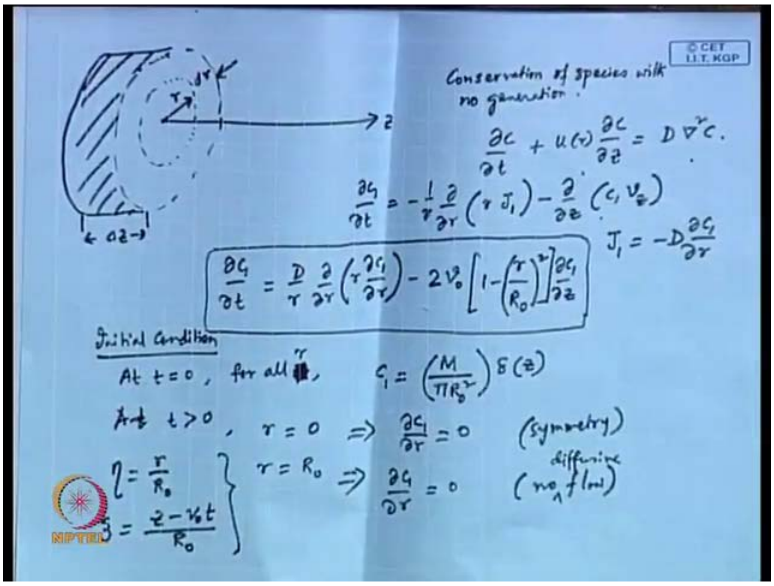

Conservation of species with no generation:

$$\frac{\partial c}{\partial t} + u(r)\frac{\partial c}{\partial z} = D\nabla^2 c.$$

$$\frac{\partial c_1}{\partial t} = -\frac{1}{r}\frac{\partial}{\partial r}(r J_1) - \frac{\partial}{\partial z}(c_1 v_z)$$

$$J_1 = -D\frac{\partial c_1}{\partial r}$$

$$\boxed{\frac{\partial c_1}{\partial t} = \frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_1}{\partial r}\right) - 2v_0\left[1-\left(\frac{r}{R_0}\right)^2\right]\frac{\partial c_1}{\partial z}}$$

Initial Condition

At $t=0$, for all r, $c_1 = \left(\frac{M}{\pi R_0^2}\right)\delta(z)$

At $t>0$, $r=0 \Rightarrow \frac{\partial c_1}{\partial r} = 0$ (symmetry)

$r = R_0 \Rightarrow \frac{\partial c_1}{\partial r} = 0$ (no diffusive flux)

$$\left.\begin{aligned}\eta &= \frac{r}{R_0}\\ \xi &= \frac{z - v_0 t}{R_0}\end{aligned}\right\}$$

If capital R is the radius, capital R is the radius of the tube, then you pick up a differential element which has a dimension I mean you you pick up differential element ofthisthisit is an annular shaped element. So, this annulus is basically between randrplus dr. So, this annulus we talking about and it has a depth of delta z. So, if you try to write down the differential equation or if you writetry to write down the governing equation for concentration, you I mean this we discussed in the last class, that you would be writing an equation something like this, and then you have a basically what you are accounting here isthe convection in the axial direction,that meansconvection in the z direction and diffusion in the radial direction.That is what you are looking at.

So, del C 1 del t is equal to this so, this is the this is the final equation that we arrived at right.This is the this is the result of diffusive term that means, radial diffusion and this is the result of convective term.Convective term in a sense thisthis part 2 V 0 into 1 minus r by R 0 whole square, this term is basically the velocity, local velocityand that V del C 1 del z this is the convective term.

So, V naught is the average velocity and 2 V naught is the maximum velocity and this thisyou know it is it comes from a standard expression for parabolic velocity profile. So, this is the governing equation and at that time I pointed out to you, that the initial condition is at t equal to 0 for all r,this concentration is given as M by pi R 0 squaredelta z.That means, you are assuming that at time t is equal to 0you are introducing introducing at t equal to 0you are introducing at the inlet a Dirac function. I mean you are you are introducingintroducing a spot of tracer at the inlet.That is applicable to all r and then at t greater than 0 for t greater than 0, you you have assumed thatat r is equal to 0, del C 1 del r equal to 0, which arises from symmetry and at r is equal to r 0 that means, at the wall.This del C 1 del r is equal to 0 which is arising from no flow or no diffusion no diffusive flowno diffusive flow.That means, at at the wall there isnot any diffusion taking placeso, D del C 1 del r that has to be equal to 0 or in other words del C 1 del r equal to 0. And at r is equal to 0 whatever, profile you have that has symmetry,at the symmetry along that central axis.

So, that has to be honored. So, r equal to 0 del C 1 del r is equal to 0. So, these are the boundary conditions that you have for or t greater than 0. Then you are in you have introduced two dimensionless quantityone is eta; which is equal to r by r 0that means, dimensionless radius and another is dimensionless axial distance; which you what you have done is here, you have written zeta is equal to z minus V 0 t by R 0.Z minus V 0 t is arising from the moving co-ordinate that means,you are this entire spot is moving at an average velocity V 0.So, you are accounting for that.

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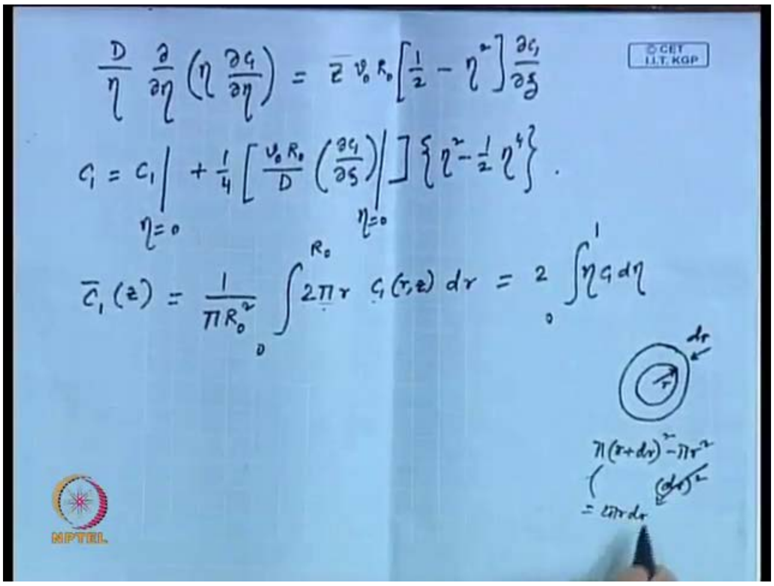

$$\frac{D}{\eta}\frac{\partial}{\partial\eta}\left(\eta\frac{\partial c_1}{\partial\eta}\right) = 2 v_0 R_0\left[\frac{1}{2}-\eta^2\right]\frac{\partial c_1}{\partial\zeta}$$

$$c_1 = c_1\Big|_{\eta=0} + \frac{1}{4}\left[\frac{v_0 R_0}{D}\left(\frac{\partial c_1}{\partial\zeta}\right)\Big|_{\eta=0}\right]\left\{\eta^2-\frac{1}{2}\eta^4\right\}.$$

$$\bar{c}_1(z) = \frac{1}{\pi R_0^2}\int_0^{R_0} 2\pi r\, c_1(r,z)\,dr = 2\int_0^1 \eta c_1\,d\eta$$

$\pi(r+dr)^2-\pi r^2$

$(dr)^2$

$= 2\pi r\,dr$

So, this is what you have at that timeand I said in the last class, that thisthisis a solution for thefor the differentialequation. D by etathis is a solution that satisfies thegoverning equation as well as the boundary conditions.And and, first of allthis is this is the converted formthe first expression that I put here is the governing equation in terms of eta and zeta,instead of writing it in terms of r and z this is written in terms of eta and zeta and then we said that this is this is one solution to this equation.And, then youthen what we discussed in the last class is that C 1 z C 1 bar z that means, we that is what we are trying to find out,the concentration averaged over the entire cross section so, ifyou try to find out the concentration averaged over the entire cross section, you have to pick up a differential element.

Annular shaped differential element find out what is the concentration. So, for that annular shaped elementthe concentration is C 1 r z, for that annulusannulus whose inner radius is r and the outer radius is r plus dr,for that annulus the concentration that you assumed is C C 1 r z.That meansthearea over which this concentration applies is 2 pi r C 1 r so, 2 pi r dr if you if you have an annulus, we were talking about. So, this is r and this is drso, you are talking about thisso, ideally this should be, what this should be pi r plus dr whole square minus pi r square that is the area of this annulus and if you ignore this d r whole square term,if you ignore if you ignore this dr whole square term with assumption that dr is small then you can write this expression is equal to 2 pi r dr.

So, that is the area of this annulus so, you are multiplying this area, annulus area with the corresponding concentration and you are integrating all such products from 0to R 0 and then finally, you are dividing by the entire area of the circle pi R 0 square.So, that is how you are getting the average concentrationwhich is C 1 bar zall right. So,this C 1 bar z is equal to 2 into integration 0 to 1 eta C 1 D eta. All right so,with so, this is this is what you get as C 1 bar. Now here, you make an assumption the assumption is like thisthe assumption is like this, that you are assuming del C 1 del zeta that is equal todel C 1 bar del zeta. This is an assumption you make at this point,because this will help treating del C 1 del zetaas independent ofr.

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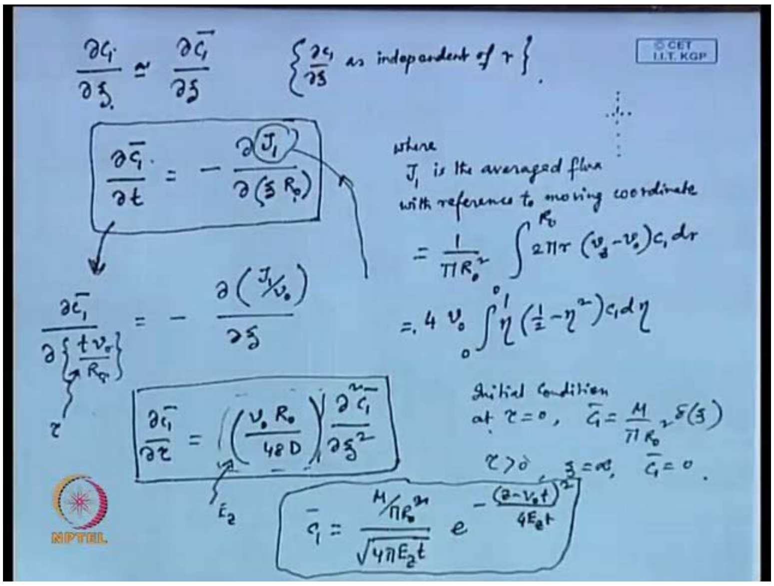

$$\frac{\partial c_1}{\partial \zeta} \simeq \frac{\partial \bar{c}_1}{\partial \zeta} \qquad \left\{ \frac{\partial c_1}{\partial \zeta} \text{ as independent of } r \right\}.$$

$$\boxed{\frac{\partial \bar{c}_1}{\partial t} = -\frac{\partial J_1}{\partial (\zeta R_0)}}$$

where J_1 is the averaged flux with reference to moving coordinate

$$= \frac{1}{\pi R_0^2} \int_0^{R_0} 2\pi r (v_z - v_0) c_1 \, dr$$

$$= 4 v_0 \int_0^1 \eta \left(\frac{1}{2} - \eta^2\right) c_1 \, d\eta$$

$$\frac{\partial \bar{c}_1}{\partial \underbrace{\left\{\frac{t v_0}{R_0}\right\}}_{\tau}} = -\frac{\partial (J_1/v_0)}{\partial \zeta}$$

$$\boxed{\frac{\partial \bar{c}_1}{\partial \tau} = \underbrace{\left(\frac{v_0 R_0}{48 D}\right)}_{E_2} \frac{\partial^2 \bar{c}_1}{\partial \zeta^2}}$$

Initial Condition

at $\tau = 0$, $\bar{c}_1 = \frac{M}{\pi R_0^2} \delta(\zeta)$

$\tau > 0$, $\zeta = \infty$, $\bar{c}_1 = 0$.

$$\boxed{\bar{c}_1 = \frac{M/\pi R_0^2}{\sqrt{4\pi E_2 t}} \, e^{-\frac{(z - v_0 t)^2}{4 E_2 t}}}$$

So, this is this is the advantage that you want to make,that is the advantage that you want to take and to take this advantage what you write here is del C 1 del zeta is equal to del C 1 bar del zeta. What does this mean?I mean do you do you have a much of an idea what what this could be?Zeta is already in moving co-ordinate. So, at a particular zeta zeta is already in terms of moving co-ordinate. So, thethe change in concentration in direction zeta can be,expressed as change in the average concentration with reference to zeta that is that is what your making here.

So, this is with this assumption what you what you can write in this case is that the you are you are then in that case you can write this as,del C 1 bardel t is equal to minusdel g 1 del of zeta R 0 where,g 1is the averagedflux with reference to movingcoordinate, that meansis equal to 1 by pi R 0 square integration 0 to R 0 2 pi r V z minus V 0 C 1 dr,which which happens to be equal to I mean let me give you the final expression first, 4 V 0 integration 0 to 1 eta into half minus eta square C 1 D eta this is the final expression. So, what you have here is that(no audio from 15:36 to 17:42) so, what what you are having here is you are basically solving this equationinstead of writing it in terms of in terms of C alone, you are writing it in terms ofin terms of C 1 bar.And since, you are writing in term of C 1 bar this g 1 that also has to be averaged and this is how the g 1 would be averaged, in that case. So, what you do here is you then you would be writing this as this expression, first of all these expression will take the shape, del C 1 bar and instead of del t you club some of the terms because you you are bringing theseso, when when you are this g 1 would be replaced by this whole thing you you have this this g 1 would be replaced by this expression that you have.

So, this g 1 would be replaced by this term hereso, what you do here is instead of del t you write del t V 0 by R 0 and call this tau.This is equal to minus del of J 1 by V 0del zeta. It is nothingnothing I mean you you have divided see, here you have included a V 0 and R 0 which would be, which has already this R 0 was coming from here and this V 0 has been added here. So, this is how you are doing it. So, this left hand side you are calling it this left hand side you are calling it del C 1 bar del tau, because tau is this quantity t V 0 by R 0 this quantity is called tau.So,del C 1 bar del tau and this is equal to on the right hand side you have to replace this g 1 by this quantity so, what you would end up with is V naught Rnaughtby 48D del square C 1 bar del zetasquare.

So, this isthis is the expression that you will have in that case.And this expression will havenow you will you will impose those initial and the boundary conditions, the initial condition is that at tau is equal to 0 for all zeta, C 1 bar is equal to M by pi R 0 square delta zeta and for tau greater than 0 zeta is equal to infinity C 1 bar is equal to 0. So, with that you willyou will solve this equationso, then it would this these term can be simply replaced.This is in fact, the E z term that you have looked in. So, you thisthistreatment would be very similar.

So, the treatment would be very similar to the onethat you had, forfora diffusion of a spot of dye in an infinite medium instead of D,you have this E z term appearing.And so, you have the solution which we had earlier, we have written it earlier that M by pi R 0 squaredivided by square root of 4 pi E z te to the power minus of z minus V 0 t whole square divided by 4 E z t. So, this isthis is the this is the term that you had we we have we have already seen this expression before, but now at least we have identified the thegoverning equations and the boundary conditions that are leading to this expression.Once again, I point out that for thisexpression, you have M is equal to total solute in the pulse, R 0 is equal to tube’s radius, z is equal to distancealong the length of the tube,V naught is equal to fluid velocity, t is equal to timeand E z is equal to dispersionE z is equal to dispersion coefficientthat is equal to R 0 V 0 square divided by 48 D.

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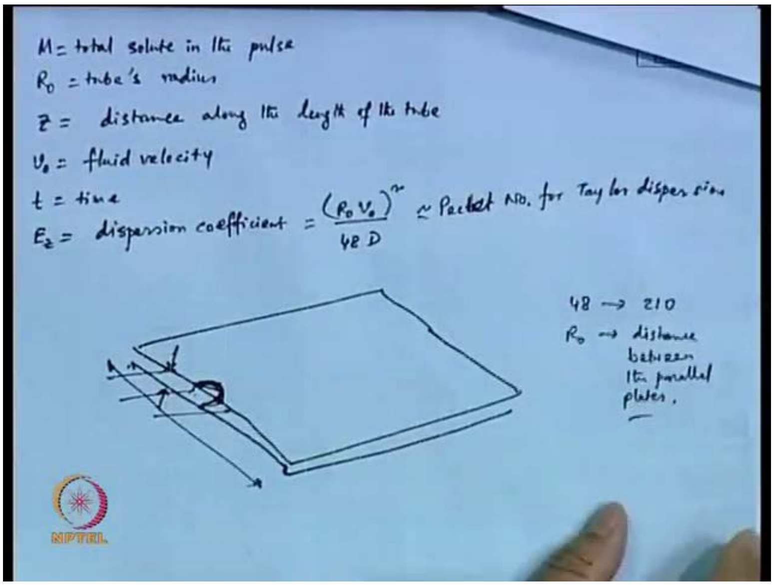

M = total solute in the pulse

R_0 = tube's radius

z = distance along the length of the tube

V_0 = fluid velocity

t = time

E_z = dispersion coefficient $= \frac{(R_0 V_0)^2}{48 D}$ ~ Peclet No. for Taylor dispersion

48 → 210

R_0 → distance between the parallel plates.

This is considered equivalent to Peclet number for Taylor dispersionTaylor dispersionPeclet number forTaylor dispersion.So, these are the these are the terms that you have and with that this is the expression that you had, we have written it already.This expression, I have pointed out before that this expressionthis has all the inherent features of diffusion of spot of dye in infinite medium, but what you needed todo at this here, I mean if we if we try to quickly recap on what we have done.We made an assumption here that del C 1 zeta is equal to del C 1 bar del zeta.

That means, the change in concentration in the z axis, when you are considering you are in with the moving coordinate system that you are treating as same as the change in average concentration,in the same same zeta axis. So, by doing this what you are doing is del C 1 del zeta has become independent of r so, that feature you are you are taking into account. And then you are writing it, writing that basic governing equation that del C 1 bar del t is equal tothis quantity minus del J 1 del zeta R 0 this is how? So, this is this becomes yourgoverning equation I should say in terms of C 1 bar now. You are talking about a diffusion you are talking about change of C 1 bar with t and why C 1 bar is changing. I mean think of it, I mean now we do not have the dependence of radial direction. So, radial part is completely taken off.

The moment seethis is the advantage of these these this condition, you have written del C 1del zeta is similar to del C 1 bar del zeta.Moment you write this then what you would be doing is you would be doing entire analysis in terms of C 1 bar and this radial axis is completely gone.You you have already incorporated whatever, you are suppose to do, in the radial direction and now you are talking about the averageconcentration over the entire cross section.And now, that average concentration over the entire cross section that is changing with time and that is changing with time because there is convectiveconvective flux, in axial direction that means, in z direction and that convective flux. So, that is expressed here del J 1 deldel J 1 del zeta r 0. So, it isit is entirelydone in the moving coordinate system see, this zeta R 0 means what?Zeta R 0 is z minus V 0 t.

So, you you are differentiating with reference to moving coordinate. So, J 1 also has to be defined with reference to moving coordinate and J 1 is the average flux over the entire cross section. So, that is what you are finding out here.1 by pi R 0 square that is so, so, what you are doing again?Annular area is 2 pi r dr that you know. 2 pi r dr V into CV into Cinto this area.Now, thisthis since, you are talking about the moving co-ordinate system it has to be V z minus V 0. So, you are as if I mean you are co-ordinate system is moving and from that average location what is the flux?Then coordinate system has moved here, but what is the flux? Then coordinate system has moved here and what is the flux? So, that is exactly what you are doing becauseyour coordinate system itself is moving you have already compressed thatyou have you have already taken care of that radial part you are working with the average concentration and you are trying to find out how the average concentration changes with reference to zeta, mind it not z zeta.

Zeta is in moving co-ordinates system. So, any J 1 bar because of this convictive flux that J 1 bar has to be calculated with reference to this this moving coordinate system. So, that is how we have we have written here the J 1 bar. So,so, J 1 is the average flux and that is how we are written it here and that J 1 appears here now, you are doing this is your modified governing equation.This is the modified governing equation that you are doing with C 1 bar and J 1. So,so, now, you are solving this equation. So, to solve this equation you have simplified this here you have written it in terms of tau and bringing this J 1put this here,solve this here and bring it there and you will end up with this governing equation and what you see basically here is, it is same as the one that you had earlieronly thing is instead of diffusion coefficient you have this term; V naught Rnaught by 48 D. So, this is this you are calling as, E z the dispersion co-efficient and you are proceedingwith proceeding with this as before.

Now, we have we have talked about this circular cross section that means, we had we talked about a capillary here, we were talking about a circular capillary.Now, if you do not have a circular one, instead if you have flow between two parallel plates.Flow between two parallel platesthen in that case this 48would be replaced by 210.I mean people have already done this analysis, thisTaylor dispersion this is originallydone byTaylorthen it was it was modified by other researchers, they have they have done this entire exercise for flow between two parallel plates. So, not in a circular cross not for a circular cross section and they found that this 48 becomes equal to the factor 210 and this R 0 will replaced by the distance between tow plates.

So, if somebody is working with a non circular cross section still, there will be Taylor dispersion of course, I mean if thisthisthe with the the dimensions one has to be much higher than the other, I mean when when we talk about two parallel plates, flow between two parallel plates the distance between two parallel plates is much smaller than the width of the channel.So, one is height another is width if I put it then height must be much less than the weight and we working with this. So, so you have the dispersion in the in in that that between the two parallel plates I mean do you understand what I am trying to say.If you have if you have two parallel plates that means, this is a platethis is a plate and this is another platethis is another plate. So, you are having a flow through this. So, naturally the in any parabolic distribution or in any any sort of distribution that will happen between these two plates. I mean we are we are talking about we arewe are interested in this dimension.This dimension does not matter to us.

So, this dimension this this distance between two parallel plates that would be replaced by R 0 that is what I am trying to say. If,somebody is working with a non circularone then instead ofinstead of R 0 you will beyou will bereplacing it by the distance between two parallel plates.Not the of course, for a non circular channel there is another dimension here, but that dimension would not be would be in consequential here for this purpose.All Right so, this is this is something which you need to,in you need be aware that this 48 would be changed to 2 1 0 and Rnaught would be changed to distance between the parallel plates.

If, it is a square channelit has to be figured out somebody has to figure out. I mean I am notaware of what should be the numbers or how it is to be.But that can be done I mean I am suresome researchers already done it, I mean it is just I am not aware of it. So, this is this is what we have as far as the,this thing is concerned, as far as the as far as thediffusiondiffusion is concerned,as far as the Taylor dispersion is concerned.The next topic that I pick up is the Chromatography inina microchannel.

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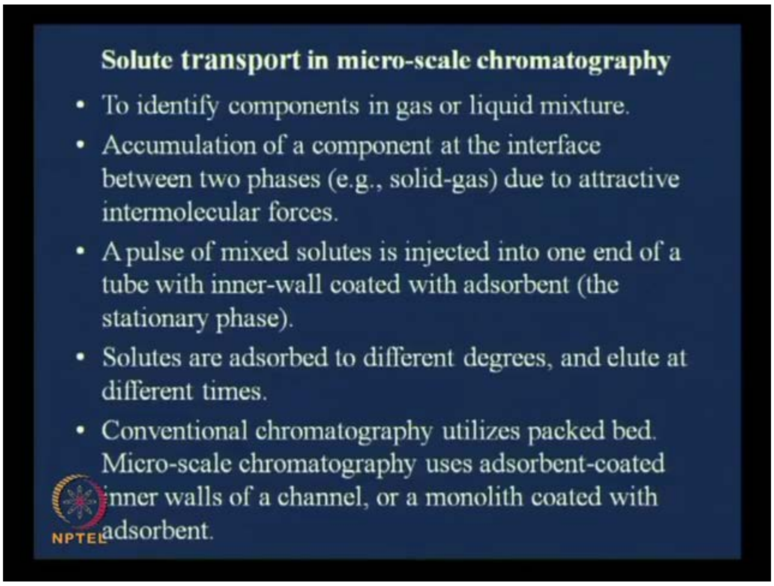

Solute transport in micro-scale chromatography

- To identify components in gas or liquid mixture.
- Accumulation of a component at the interface between two phases (e.g., solid-gas) due to attractive intermolecular forces.
- A pulse of mixed solutes is injected into one end of a tube with inner-wall coated with adsorbent (the stationary phase).
- Solutes are adsorbed to different degrees, and elute at different times.
- Conventional chromatography utilizes packed bed. Micro-scale chromatography uses adsorbent-coated inner walls of a channel, or a monolith coated with adsorbent.

Basically, ifI if Ilook at if I look atwhat we have here in thisin thispower point slide. We here, we describe solute transport in micro-scale chromatography, they the objective of this is to identify components in gas or liquid mixture that is what the main main purpose here.What you look at here is the accumulation of a component. So, you are introducing a sample that has component A, B,C, D and what you are looking at is the accumulation of a component;accumulation of a component means either A or B or one of the components. Accumulation of a component at the interface between two phases such as, the solid gasdue to attractive intermolecular forces so,accumulation of a component at the interface between two phases, solid gas where where are you getting these two phases.So, you have a tube or you have a non circular channel and thenyou have the wall of the, inner wall of the channel coated with an adsorbent material.

So, some components,one one of the components or may be more than one componentsthey would accumulate at the interface accumulate on the wall thatthat absorbent layer that you put that is a solid adsorbent. So, the interface between solid-gas is at the wall. So, there the accumulation takes placeand this accumulation is due to attractive intermolecular forcesnow, if a pulse ofmix solutes is injected into one end of a tube with inner wall, coated with adsorbent, which is called as stationary phase in this context.Then the solutes are adsorbed to different degrees and elute at different times.Solutes are adsorbed to different degrees and elute at different times.Now, theconventional chromatography utilizes packed bed,micro-scale chromatography uses adsorbent coated inner walls of a channel or a monolith coated with adsorbent.

Why whyfirst of all why something adsorbs?Why something gets adsorbed on the wall? And why something will get dissolved also? I mean, because you are I am saying that a pulse of mixed solute is injected into one end of a tube with inner wall coated with adsorbent. That I amI am referring it as stationary phase.And then I am saying solutes are adsorbed to different degrees and elute at different times.So, I hope yousince,we have a mixedcrowd here, I hope you understand that thereand adsorption and then desorption both the process both the processes can happen simultaneously.

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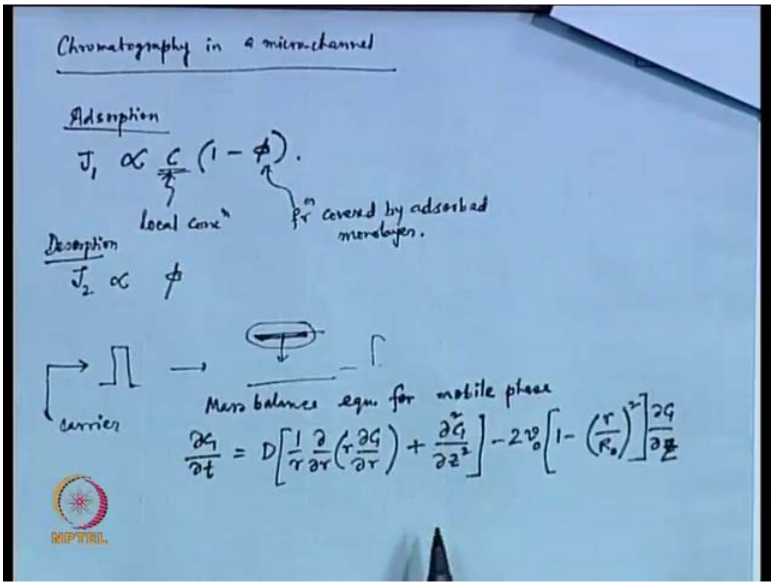

Chromatography in a micro-channel

Adsorption

$J_1 \propto C(1-\phi)$.

local conc^n

fr^n covered by adsorbed monolayer.

Desorption

$J_2 \propto \phi$

carrier

Mass balance eqn. for mobile phase

$$\frac{\partial C}{\partial t} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)+\frac{\partial^2 C}{\partial z^2}\right]-2v_0\left[1-\left(\frac{r}{R_0}\right)^2\right]\frac{\partial C}{\partial z}$$

What what I mean by this isthat in case of an adsorption; the flux of molecules moving from the gas phase to the solid phase that is given as J 1, which is proportional to C into 1 minus phi what is C? C is the local concentrationC is the local concentration of that particular solute. So, if you are if you are injecting the gas phase into this micro channel. Then the local concentration of component A, which is being adsorbed in the gas phase.That is what is referring asis referred as C.And what is phi?This phi is fraction covered by adsorbed monolayer.

So, what is what is this?So, you have a forward flux this is called a forward flux.Similarly, there would be a backward flux, which would be proportional to phi alone.That means, there would be a forward flux, which we refer as adsorption and the second one, we can probably call this as desorption. So, there would be a forward flux that forward flux means; the flux of molecules from the gas phase to the solid phase. So, naturally that flux would be higher, if you have higher number of component a present in the in the gas phase. And also, the amount of covering that has take because if the if theabsorbedif the stationary phase which is the solid adsorbent if it is holding it is because of intermolecular forces it is holding the solid sample the component A on the surface.

If thatsurface is already covered.If the surface is already covered then there would be I mean. So, you you will consider the surface to be completely saturated. So, there it cannot hold any more component A. So, how much remains unoccupied?That is important also. So, that is what is defining the forward flux. On the other hand how much has been occupied that is forcing a backward flux.It is it is forcing at desorption. So, there is anthere is an interplay between these adsorption and desorption that that you must understand. So, when you are putting a mixed solute, I mean you putting a pulse of A B C D depending, I mean now some are getting adsorbed more,strongly some are not getting adsorbed. So, you have you have a mix mixture of thiscomponents, you have A B C D and that is flowing through the channel.

Some are getting adsorbedand then then. So, so you have a concentration presentso, what you what you have done, you have given a pulse and that is flowing through the channel. So, so this wall it is it is seeing a high concentration of component A which is supposed to be adsorbed. So, naturally that will be adsorbed there would be huge forward flux and that would be adsorbed.And the pulse flows downstreamRight so, if there is a pulse of this A B C D and then you are havinga carrier fluidcarrier fluid. So, that carrier fluid is pushing this pulse. I am talking about Carrier this so, typically it is an inert gasfor a gas phase system. So, this is pushing itdown.

So, once this pulse is gone, what will happen to this adsorbed layer?Then it will start desorption,because it is no the C is not there. So, C is not pushing the forwardflux. So, there would be a backward flux. So, this is coming back to the system. So, you will be finding the all this A B C D they are eluting, they are coming out at the outlet, but at different times depending on this dynamics or this adsorption desorption. So, that is that isthe well idea.Now since, I saidI said that here also you are you are resorting on a very thin channel and so, you would be you would be having a very similar mass balance equation as you had, in case of a Taylor dispersion. So, the mass balance equation if you if you write the mass balance equationmass balance equation for mobile phase what is a stationary phase?That solid adsorbent and the mobile phase is that pulse that you have given, which contains A B C D carried downstream by the inert gas. So, that systemthat system you are call you are referring as mobile phase.

So, if you try to write down the equation,it would be something like this del C 1 del t. 1 is the species one, we are talking about out of A B C D,we are talking about or out of which is 1 23 4, we are talking about species one, you would be having it is a the first term is already known to you first term is known to you.The second term is a new thing we are talking about an axial diffusion.If you are having a long channel, probably it is wise to have the axial diffusion also to be considered earlier in case of a tailor dispersion what you have considered is basically the axial convection and radial diffusionAll Right. Here, you this is that axial convection term, 2 V 0 this is the velocity term V del C del z that is that axial convection term, it is still there.

Here, you havethis is the radial diffusion term this is still there D into this. Another term is additionally there which is which was additionally here, which is not there in theTaylordispersion is D del square C 1 del z square this term.This is this is due to axial diffusion. So, this is this is the governing equation thatresearches have considered forchromatography; however, this is only for the mobile phasethis is only for the mobile phase what you have is another differential equation for this adsorbent phase.

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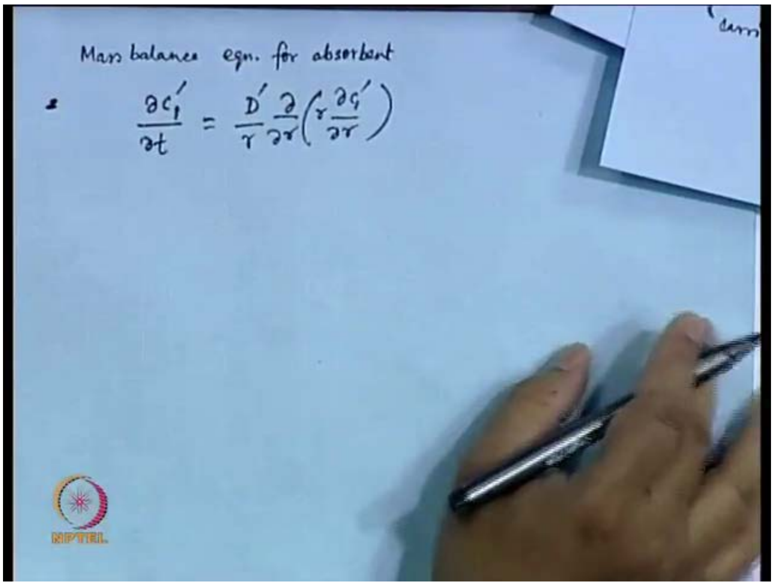

Mass balance eqn. for absorbent

$$\frac{\partial c_1'}{\partial t} = \frac{D'}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_1'}{\partial r}\right)$$

So, you are writing the second mass balance equation, mass balance equation for the stationary phase you call it oryou can call it for adsorbent. So, one for the mobile phase and another for the stationary phase,you are writing it here, whatwhat all you are concentrating here?Here let me, write the equation first it would be del C 1 prime del t, what iswhy I am bringing a prime here, one is species one, I have pulse containing 1, 2, 3, 4, I amtalking about one, species one here.

Prime means the concentration inside thesolid phase. So, that is why I am writing it as prime,this is equal to D prime bybyr del del r of r del C 1 prime del r. So, what you are considering here is only radial diffusion, no axial no axialconvection, because axial convection is not possible within a solid phase,within a solid phase axial convection is not possible.Axial conduction that is oror you are talking about axial diffusion; axial diffusionis not considered here because there would be the concentration gradient in the axial direction within the adsorbent phase would be negligible.The concentration gradient of species, within the adsorbent phase in the axial direction that concentration gradient is negligible. So, axial diffusion is not important here.

So, only thing that you consider is radial diffusion.Do you do you understand what kind of diffusion it would be? I mean within the adsorbed medium, I mean it is it is not not a kind of I meanthe moment we said diffusionthewhat what comes to our mind isthatsmoke diffusing, I mean you have a small candle here and the smoke is diffusing here in this medium or you have a beaker full of water, and you are putting a drop of ink and that is diffusing.So, diffusion insidethe solid diffusion inside the solid,so it it would have a different kind of diffusion coefficient. But you you might you must have already seen diffusion in catalyst. I mean those those who are who have, I mean any any reactionanybody who studied reaction engineering, you have a term diffusivity in catalyst.

So, diffusion coefficient inside a porous solid is not something, which is new to you. But one thing, you must understand is that this diffusion coefficient would be probably order of magnitude different from a bulk diffusion coefficient, in a liquid or in a gas. So, that has that has to be kept in mind. So, that is why in fact, I put this D prime. So, D prime isdifferentyou you canyou can probably get a quick feel of thisthis diffusivity is typicallyit would be the bulk diffusivity,multiply I mean, that means, the diffusivity in a gas phase multiplied by the curiosity factor. I mean you have a porous network of this adsorbent that has afactor that you have to multiply.

So, it would be definitely you know that it will be an order of magnitude or more different. So, that is why you call it D prime. So, there would be only radial diffusion, axial diffusion you know that concentration gradient is not importantso, that part is gone. So, this is the only mass balance equation that you have for the absorbent phase. Now, if we try to look at if we try to look at thetheboundary conditionsthen the boundary conditions for these one would be, for the mobile phase, boundary condition would be t is equal to 0 t is equal to 0. You have for all r you have C 1 is equal M divided my pi R 0 squareinto delta z. You have given a small pulse at the inlet.

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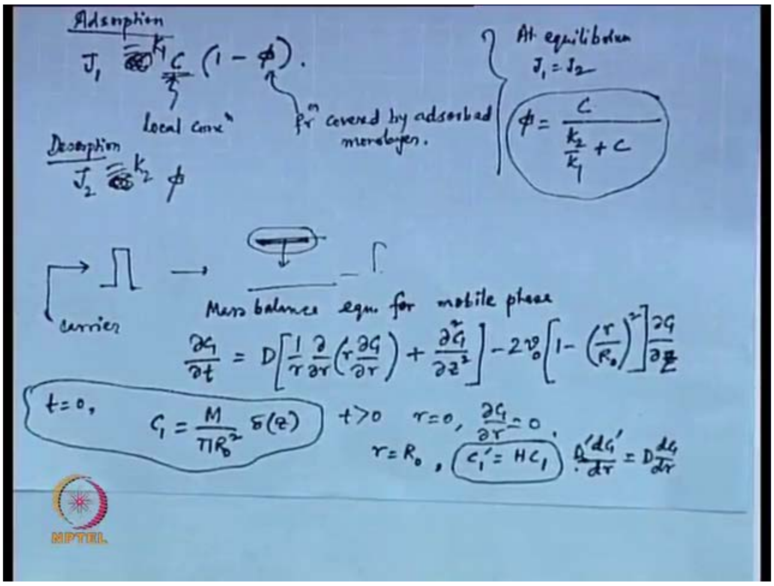

Adsorption

$J_1 \propto k_1 C (1-\phi)$.

local conc^n

fr^n covered by adsorbed monolayer.

Desorption

$J_2 \propto k_2 \phi$

At equilibrium

$J_1 = J_2$

$$\boxed{\phi = \frac{C}{\frac{k_2}{k_1} + C}}$$

carrier

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$$\frac{\partial C_1}{\partial t} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_1}{\partial r}\right) + \frac{\partial^2 C_1}{\partial z^2}\right] - 2v_0\left[1-\left(\frac{r}{R_0}\right)^2\right]\frac{\partial C_1}{\partial z}$$

$t=0$, $C_1 = \frac{M}{\pi R_0^2}\delta(z)$

$t>0$ $r=0$, $\frac{\partial C_1}{\partial r}=0$.

$r=R_0$, $\boxed{C_1' = HC_1}$ $D'\frac{dC_1'}{dr} = D\frac{dC_1}{dr}$

So, this would be the C 1, this is one condition, this you call it initial condition and for t greater than 0 at r is equal to 0 symmetry has to be there. I mean there is you have not done anything if you have a circuit if you have a channel of circular cross section and if you coated the wall uniformly, then you have no reason to believe that symmetry has been sacrificed.So, at r is equal to 0 del C 1 del r would be equal to 0 that is known.And then you have another condition that at r is equal to r 0 that means, at the wall at r is equal to R 0,you write there would be some continuity in concentration and that continuity would be written as C 1 prime is equal to H C 1 that is one thing. And the otherthing is D prime dc one prime dr that is equal to D dc 1 dr.

Do you under I mean I am talking I will talk about this this is this ispeople fromchemical engineering background this H is similar to that henrys constant typeterm, but that that is that is not I mean I willI will explain to you what what is a basis for this H? But first focus on this part, the D prime dc 1 prime dr is equal to D dc 1 dr.You got to understand the fact that whatever, is arriving by radial diffusion whatever is arriving byradial diffusion at the wallthat has to go into the solid phase. So, you have to have the continuity of the flux maintained, at the wall at the wall you have the adsorbent and at the interfacethe continuity of flux, has to maintain. So, whatever is approaching the wall with a diffusive flux from gas phase side, has to be equal to thethe diffusive flux that is penetrating into the solid phase. So, that is exactly what this boundary condition says. D prime dc 1 dr that is equal to D dc 1 dr.At r is equal to r 0that means, at the wall.

All Right so, this is one condition that you must appreciate, this one is by symmetry you know we have not sacrificed the symmetry.This one is bybythat continuity of flux at the interface of absorbent and the mobile phase. So, this is understood and how do you explain this part? C 1 prime is equal to H C 1.If we go back to theseexpressions if we go back to this expressions one thing you can say is that at equilibrium at equilibrium,you will write J 1 is equal to J 2.And if you write, J 1 is equal to J 2 you would be writing then now you will have a constant because because you know that though we have written these expressions though we have written these expressions, I have to have a constant term here and that constant term is defining, which species will be adsorbed more and which species will be adsorbed less.

So, for J 1 is equal to J 2 you can write if if you put the if you equate this two, we would be end up with phi is equal to C divided by k 2 by k 1 plus C.That means, the layer that is being the fraction that is covered that is equal to C divided by k 2 plus k 2 by k 1 plus C this is this is what you will end up with. So, what you are assuming here is that the concentration in the solid phase is equal to it depends on the concentration in the gas phase in a linear manner; that means, these there there exists a linearity between these two concentrations. I mean you you can youit it may be itit is an assumption, you you are making an assumption, but the objective of this is toone one good reason for taking this assumption is that.

They they people have come up with an analytical the researchers have come up with an analytical expression for this whole system of equations; that means, you have once one equation for the moving phase, another equation for the stationary phase and with this boundary, I mean I have not talked about the boundary condition for the solid phase yet.We are just we are still in the boundary condition in the moving phaseso, for thiscombinedform of equations people have the researchers have come up with an analytical expression very similar to the one which we had done for Taylor dispersion. So, by by accounting this linearity hear and and the reason for this linearity, I can see here is that at equilibrium, I canI can have this phi is equal to C divided by this quantity All Right.

So, depending on this value depending on depending on this value you canyoucan come up you can you can have this the linearity established. So, this is this is what you have here.

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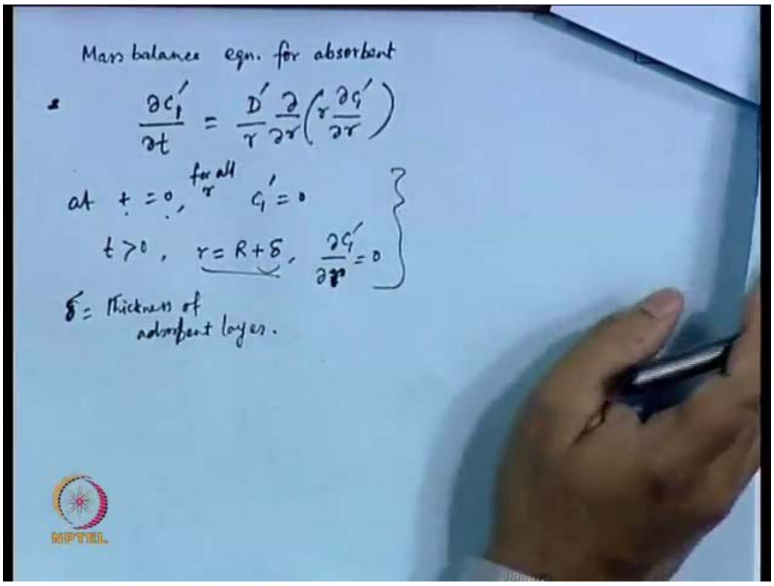

Mass balance eqn. for absorbent

$$\frac{\partial c_1'}{\partial t} = \frac{D'}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_1'}{\partial r}\right)$$

$$\left.\begin{array}{l} \text{at } t = 0, \overset{\text{for all}}{r} \quad c_1' = 0 \\ t > 0, \quad \underbrace{r = R + \delta}, \quad \frac{\partial c_1'}{\partial r} = 0 \end{array}\right\}$$

δ = Thickness of adsorbent layer.

Now, if I try to write quickly the boundary conditions for thesolid phase, what you have for the solid phase is at t is equal to 0 for all r C 1prime is equal to 0, for all r. C 1 prime is equal to 0, and t greater than 0 r is equal tor plus delta del C 1 prime del z is equal to 0 del C 1 prime del r is equal to 0,where you have del C 1 prime del r is equal to 0, and delta is equal tothe thickness of absorbent adsorbent layer;this delta is equal to the thickness of the adsorbent layer. So, at the end of the adsorbent layerat the end of the adsorbent layer, no diffusive flux is possible. So, that is that is one boundary condition you have.And at t is equal to 0,adsorbed adsorbed layer is completelyit is it is just a native layer,no nothing nothing has penetrated into it.

So, this is the boundary condition that you have there. So, you have a mass balance equation for the adsorbent phase with some boundary condition, you have a mass balance equation for the mobile phase with some boundary condition.And then thisthe researchers have come up with a solutionin fact, analytical solution solution, numerical is I mean still possibility, but analytical solution is available and the advantage of this is then if at you can express it in a similar manner and come up with an E z term.Then you can probably see the effect of various parameters on the E z term.That is that is good I mean then you canyou can get a feel for these terms,how they influence thespreading of this front in a or spreading of this pulse in a micro micro-scalein a micro channelin a in a chromatographic system operating in a micro channel. So, we will get to the final expression and the importance of various terms this time with the, I mean it is not possible for getting into detailed derivation.

I just give you the final form and the importance of various termsin the next class.That is all for today.