

**Mechanical Unit Operations**  
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**Lecture 30 - Cross Flow Filtration - 2**

Welcome to the MOOC's course Mechanical Unit Operations. The title of this lecture is Cross Flow Filtration Lecture Number 2, on this cross flow filtration. We have already seen a basic, a few basic things about the cross flow filtration and different types of membrane, membrane properties, those kind of things we have seen in our previous lecture. Now we are going to see a few more details about the cross flow filtration, especially with respect to ultra-filtration. So we will be developing some equations for the flux, permeate flux, concentration, polarization etc for the case of ultra-filtration membranes.

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**Permeate flux of UF**

- Performance of a membrane can be characterized by
  - permeate flux
  - % rejection
  - concentration of solute in the retentate stream
- Because of membrane fouling, the permeate flux often decreases whereas the rejection may increase
- Consider we will performance of clean membrane in purifying solutions with significant osmotic pressure

So permeate flux of ultra-filtration membranes, so the performance of a membrane in general can be characterized by three important points. First is the permeate flux. Second one is the percentage rejection of the solutes by using the membranes and third one is the concentration of the solute in the retentate stream, because here in the membranes we, one of the phase you know retentate phase becomes more concentrated compared to the feed.

So what is the concentration of the solute in the retentate stream is also kind of important factor as we are going to discuss. We are going to find out each and every detail of these things now in this particular lecture. So, because of membrane falling the permeate flux often decreases

whereas the rejection may increase. What happens you know when there is a kind of membrane surface here, along with, you know, when a kind of feed which is having small particle, a low concentration solution which is feed is here nothing but a solution having low concentration of particles and particle sizes are also in general very small of order of microns or even less; then only we use this cross flow filtration using membranes.

So when this operation is taking place then what happens, some of the particles will be deposited on the layer and then they form a kind of a very thin gel kind of layer here, very thin gel kind of layer would be there, right. Because of that layer, additional resistance to the flow of permeate to pass through this membrane would be there. Membrane resistance is already there, and then because of that one there is a kind of some permeate flux but and in addition to this membrane resistance the gel layer whatever the particles they are forming on the surface during the process of, you know membrane separation, so this gel layer will also be offering additional resistance.

Because of that one, permeate flux would be reduced but however more resistance is this and more particles would be retained towards the retentate site, so then the rejection may also increase. Now what we consider? We consider performance of a clean membrane used for purifying a solution, a solution having certain amount of osmotic pressure, okay? So this osmotic pressure, you know is function of concentration as we understand.

So as the concentration of the solute increases the osmotic pressure of the feed solution whatever is there, that increases. Okay so then you know accordingly the correction has to be made in the performance. So all those things we are going to see now here.

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- Water is assumed to pass by laminar flow through the pores of selective membrane layer
- Driving force is  $\Delta p - \Delta \pi$  and  $\epsilon$  is void fraction of membrane
- Pores are not of uniform cross section and are often interconnected, thus nominal thickness of active layer  $L$  is multiplied by a tortuosity factor  $\tau$
- Applying above simplifications to Hagen-Poiseuille eq. to get superficial permeate velocity normal to surface:
 
$$\frac{\Delta p}{L} = \frac{32\mu v}{D^2} \Rightarrow \frac{\Delta p - \Delta \pi}{L\tau} = \frac{32\mu(v/\epsilon)}{D^2} \Rightarrow v = \frac{(\Delta p - \Delta \pi) D^2 \epsilon}{32\mu\tau} \Rightarrow (1)$$
- Units of the flux:  $m^3/s, m^2, m/s$ ; but more often  $L/m^2h$

Now let us assume the water is flowing through porous structure of the selective membrane layer within the laminar flow, not necessarily assuming because in general whatever the flow is there through the membrane that permeate flow rate is in general very, very small. So the Reynolds number would be in general very small.

So under such conditions, laminar flow conditions or equations related to the laminar flow can be happily considered. And the driving force here for the performance whatever we are trying to develop, performance equation we are trying to develop for the membrane, for that case driving force is not just the pressure drop but the pressure drop minus osmotic pressure because we are taking a case where the solution is having a significant amount of osmotic pressure and epsilon is the void fraction of the membrane. So membrane in porous structure is the, whatever is the porous structure void fraction is there, so that is  $\epsilon$ .

In general pores are not uniform across section and then often they are interconnected as we have seen several cases. Because of that one, whatever the nominal thickness of the active layer, so let us say if this is the active layer, you know, these active layers are in general in a few micron sizes, but just to explain I am writing, I am drawing a kind of thick layer so that we can see the detail.

So this here, this, this is the active layer, membrane layer. This is mounted on a kind of support, it is a supported membrane kind of thing. And the support is a kind of a macro porous material, okay. Now here, you know these pores, whatever the membrane surface on which the pores

would be there, pores would not necessarily be a kind of, you know uniform pore structure something like this. It is not possible.

So they may have a kind of, you know different degrees of interconnection and then different levels of, you know, porous structure across the cross-section, then this is the  $L$  of the membrane, you know across the cross-section of this active layer as we pass on, the path that the molecule, permeate molecule is passing through the membrane that is more than  $L$  because the porous structure is not uniform like this. So because of that one, we have to multiply by some tortuosity factor  $\tau$ . It is similar as kind of what we have done in the case of flow through packed bed, okay.

So here also the pores are interconnected and they are not even, they are not uniform and then their length, the molecule may be traveling the length more than the active layer thickness. So  $L$  has to be multiplied by some factor, tortuosity factor that is  $\tau$ . Now for this case whatever the Hagen-Poiseuille equation is there, what we assume that you know we take this now  $L$  if you multiply by  $\tau$ , that  $\tau$  is taking care of the tortuosity factor.

So now we can say that these pores are, you know kind of a uniform cross-section  $L\tau$ , that  $\tau$  is taking care of the non-uniformity factor so then, through this pore, through individual pores now each pore is like this, of length  $L\tau$  and then permeate through which is coming, you know  $\frac{v}{\varepsilon}$  because there are  $n$  number of such kind of you know pores are there, right, so similarly exactly the same way that we have done for the packed bed. So these factors we have to bring into the picture in Hagen-Poiseuille equation, whatever the  $\frac{\Delta p}{L} = \frac{32\mu v}{D^2}$  is the, this is the, you know Hagen-Poiseuille equation for flow through a pipe, uniform cross-section pipe.

So then this is what we have Hagen-Poiseuille equation which is valid for a infinitely long cylinder or for the cylinder where the case  $L/D$  is very, very much higher than the, you know 1. So that is  $L$  is very much larger than the  $D$  so then it is valid. So under such assumptions, those assumptions we can also apply for the simplified case here as we have given here, right, okay but with a kind of modification this  $L$  has to be multiplied by  $V$  and then this  $v$  has to be divided by the  $\varepsilon$  in order to bring the effect of the voidage through which only the material is flowing, through which only the permeate is flowing.

When we do this one, we get this thing. So this is  $\frac{32\mu v}{D^2}$  is nothing but  $\frac{\Delta p}{L}$  and also this pressure, now whatever the resistance is driving force for the steady state, it is not a simple pressure drop but also there is a kind of effect of osmotic pressure. So that, that should also be taken care into this equation. So  $\frac{\Delta p - \Delta \pi}{L\tau}$  has to be now  $32\mu L\tau$ ,  $v$  has to be  $\frac{v}{\epsilon}$  and  $D$  is as it is, we are keeping it as it is though it is not the same as the kind of this thing, equivalent diameter kind of thing we have to write but let us not go into all those details because we are not going to simplify this equation further anyway.

So what we get here, superficial permeate velocity normal to the surface  $v$  is nothing but  $\frac{(\Delta p - \Delta \pi)D^2\epsilon}{32\mu L\tau}$ , right. So here the, from this equation though  $v$  is having the units, you know meter per second so this is the permeate flux but in general this permeate flux is also represented in terms of  $m^3/s$ ,  $m^2$ , not only just meter per second, they are just you know multiplied by some kind of factor so that you know reported in this kind of forms but more often the permeate flux is reported in terms of units  $L/m^2h$ .

So now, but if you wanted to use this equation, let us assume, you know the concentration, solution concentration so then you can find out the osmotic pressure, that is not the problem. But what is  $D$ ? The pores, this membrane is having several pores on the surface, right and then these pores are having different cross-section. So which diameter should you take? That you do not know and then in general voidage is also very difficult to find out though you have the facilities now you can find out for a given membrane, alright.

So, but it is not readily available, in a sense it is not readily available though it can be measured. And then what is the tortuosity factor? We do not know actually how much it is. In packed bed we found for some cases it is 2.1 something like that, it is appropriate one, appropriate for the laminar conditions but other turbulent conditions it may be very much higher, very much different from the laminar case tortuosity factor. So having these many ambiguities getting a reliable information about permeate flux is going to be very difficult.

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- ▶ In general it is difficult to have measurements of  $D$ ,  $L$ ,  $\epsilon$ , and  $\tau$  for use in above eq. for membrane processes
- ▶ These characteristics are incorporated
  - ▶ in membrane permeability ( $Q_m$ ), i.e., pure water flux at room temperature per unit pressure drop or
  - ▶ in membrane resistance ( $R_m$ ) which is reciprocal of  $Q_m$  as below

$$v = Q_m \Delta p = \frac{\Delta p}{R_m} \Rightarrow (2)$$

*Handwritten notes:*  $v = \frac{(\Delta p - \Delta \pi) D^2 \epsilon}{32 \mu L \tau}$

- ▶ In terms of  $R_m$  is preferred to be used as in above eq. especially when one allows for additional hydraulic resistance of gel layer that may form on surface at high flux

*Handwritten notes:*  $v = \dots (Q_m)$

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- Units of the flux:  $m^3/s$ ,  $m^2$ ,  $m/s$ ; but more often  $L/m^2h$

*Handwritten notes:*  $\frac{\Delta p}{L} = \frac{32 \mu v}{D^2}$ ,  $\tau >> 1$

So what we do, we try to overcome this, you know measurements of the  $L$ ,  $\epsilon$  and  $\tau$  et cetera and then rearrange this equation in a different kind of form. So how we can write a different form? These parameters we can, or these characteristics  $D$ ,  $L$ ,  $\epsilon$  and  $\tau$  et cetera we can incorporate in kind of, in some kind of permeability or in some kind of resistance. So, in two ways the permeate flux can be reported. So now when you report...we can report in terms of the permeability that is pure water flux at room temperature per unit pressure drop or membrane resistance which is reciprocal of  $Q_m$  as below here.

So the same equation we, whatever we have, so  $v$  is equals to  $\Delta p$  minus  $\Delta \pi$  and then something is there, right, so and then something is there that you would like to know, if you specifically the previous equation 1, we write  $v = \frac{(\Delta p - \Delta \pi) D^2 \epsilon}{32 \mu L \tau}$ . This equation now we are

writing for a pure water flux.  $Q_m$  is kind of for a pure water flux kind of condition. So for pure water if there is no solute, then there will not be any kind of osmotic pressure. So then we can write this equation,  $\Delta p$  multiplied by some constant.

So all these things are, you know, we measure, we incorporate or include in something like that  $Q_m$  that we can call it as a kind of permeability, okay. So, or if you take the reciprocal of this thing so then we can take this one as  $\frac{\Delta p}{R_m}$ .  $R_m$  is the resistance which is the reciprocal of the permeability. So the either of the way it can be written. Either of the way it can be written, okay.

But in general, you know if, if you wanted to write the same equation for the case where you are using for purifying a solution, if you have a solution there would be a kind of solute and when there is a kind of solute particles in a solvent then that, you know that overall final solution would be having some amount of osmotic pressure. So you have to incorporate that osmotic pressure also in a generalized equation and then when we are, you know doing the separation by using membrane for those solutions then you know particles will be forming a kind of gel layer, not as a kind of cake as we have seen in cake filtration but you know very thin gel layer kind of thing would be forming on the surface. So that surface, that gel layer is also offering some additional resistance in addition to the resistance due to the membrane.

So then whatever the  $R_m$  is here is, you know, is resistance due to the membrane only. There is no resistance due to the gel in this equation because this equation we have written for the pure water case. Pure water case there are no particles so there is no gel formation kind of thing. So but when you take the solution then this  $R_m$  should be added with the  $R_{gel}$  or the resistance due to the gel and then this  $\Delta p$  has to be subtracted with the osmotic pressure that is minus  $\Delta\pi$  should be added. That we are going to see.

So this equation, though we can write  $v = Q_m \Delta p$  but it is writing  $\frac{\Delta p}{R_m}$  kind of form is going to be more useful because you know wherever we have this kind of gel kind of formation things are there, so those things you know can be easily incorporated, you know. Their resistance can be easily incorporated if you are writing in the form of  $v = \frac{\Delta p}{R_m}$  form.

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► Therefore, general flux eqn. for UF:

$$v = \frac{\Delta p - \Delta \pi}{R_m + R_{gel}} \Rightarrow (3)$$

► At above room temperatures, or for a permeate that is not pure water, the membrane resistance can be corrected for the change in viscosity by:

$$R'_m = R_m \left( \frac{\mu}{\mu_0} \right) \Rightarrow (4)$$

where  $R'_m$  is corrected resistance and  $\mu_0$  is viscosity of water at room temperature

So now generalized flux equation for ultra filtration membrane should be what? It should be  $v = \frac{\Delta p - \Delta \pi}{R_m + R_{gel}}$ , right, okay. So if you use the pure water then  $\Delta \pi$  is 0. For pure water osmotic pressure is 0 for pure substance and then there will not be any kind of gel, so  $R_{gel}$  would also be 0. That would be the case of previous case of equation number 2. But if you are using this one for purifying the solution using this ultra-filtration membrane so then because of the particles in the feed, feed solution you know, there will be a kind of osmotic pressure that should be brought into the picture, so  $\Delta \pi$  has come into the picture.

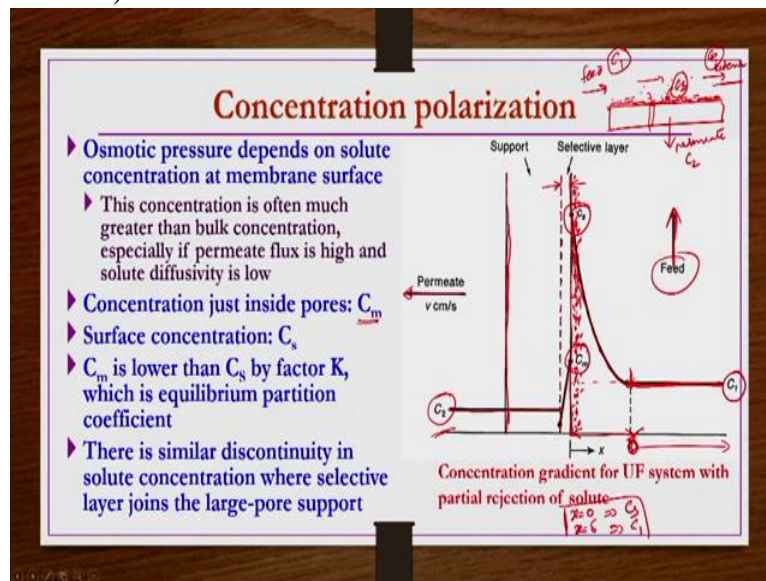
And then there will be layer of particles, fine particles forming on the surface as a kind of layer, that is known as the gel, so that would also be offering a kind of additional resistance when we are using this membrane for purifying the solution. So that resistance due to the, that whatever additional gel has formed that should also be brought into the picture, so that is here.

So if you take the pure water case,  $\Delta \pi$  and  $R_{gel}$  would be 0 and then equation 3 would be same as equation number 2 as we have just seen. But further what happens, you know the, at room temperature it is, this equation is fine, okay. But above room temperature or for a permeate that is not pure water then the membrane resistance can be corrected for the change in the viscosity. The change in the viscosity of the permeate with respect to the temperature can be brought into the picture like this.



So  $R'_m = R_m \left( \frac{\mu}{\mu_0} \right)$  where as  $\mu_0$  is a kind of viscosity of the permeate at room temperature and  $\mu$  is the viscosity of the permeate at a higher temperature at which we are operating. Remember the same equation number 3 in some books is also written in terms of, you know  $\mu$  terms will also be there. So then accordingly the unit should be changing in general. So here  $R'_m$  is corrected resistance and  $\mu_0$  is viscosity of water at room temperature or whatever the solution that we have taken.

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So now concentration polarization, concentration polarization is nothing but whatever the gel formation is there, you know, let us say this is the membrane surface active layer, okay when there is a cross flow of feed solution having a low concentration of fine particle, so this is flowing across like this. So then retentate are taken like this and then permeate is collected through bottom like this, okay. Now this is containing fine particles, so the particles are you know retained over on the surface. They are separated, right and then almost clear or almost clear permeate is collected at the bottom. This will also be having some kind of solute because 100% rejection in general is not possible.

So permeate will also be having some solute particles but very few particles, very less fraction will be there, right and then retentate, you know it is a kind of concentrated solution. So retentate concentration would be much more higher than the feed concentration.

So while this process is going on the layer of the particles would be forming as a kind of a gel here and then that will be offering a kind of a concentration which is very much higher

compared to the bulk feed concentration. Let us say bulk feed concentration is  $c_1$ , on the surface if you take concentration is  $c_s$ , the  $c_s$  is going to be very much higher than the  $c_1$  because of this concentration polarization or because these particles are forming.

So the particles are forming as a kind of gel, so that gel, you know increasing the solute concentration on the surface of the membrane, that is known as the concentration polarization. So this  $c_s$  at the surface is much more higher than the  $c_1$  and let us say permeate concentration or the solute concentration in permeate is  $c_2$ . So  $c_2$  is not 0. It is 0 only when the 100 percent rejection is there. But 100 percent rejection, it is in general not possible for any case. So then  $c_2$  will also have some values, okay. And then retentate concentration, let us say  $C$  or something like that, you know, that must be very much different.

Now because of this concentration polarization whatever the flux is there, the flux gradually decreases or the pressure drop increases, okay. And then when the pressure drop increases the  $c_s$  also increases current value, okay. So this kind of phenomena occur for ultra-filtration membrane, so this concentration polarization concept we are going to see now, and then we are going to develop equation for this case, okay. So now osmotic pressure depends on solute concentration at membrane surface.

So now what happens, if you obtain the osmotic pressure based on the  $c_1$ , so that is not going to give the correct results because the solute concentration is very much different on the membrane surface or whatever the osmotic pressure is playing role in separation, that is playing role only at the surface because membrane surface, because there only from that point only separation is taking place. So when you calculate the osmotic pressure for the solution you have to use the  $c_s$  concentration rather than the  $c_1$ , right.

So that is the reason you know, the osmotic pressure though is very small for a kind of dilute solution, dilute feed solution you take, let us say very, very small dilution like 0.01% of solids are only there in the kind of feed solution, despite of that one, so in general when you say that 0.01, you know gram per liter of solutes in a feed solution, it is kind of very small concentration. So then what you assume that osmotic pressure is going to be very small. That can be neglected.

But because of this concentration polarization what will happen? Now, the  $c_s$  is going to be much more higher. It is going to be much more higher than 0.01. How much higher, that is what we are going to develop equation to obtain this expression. So even for the dilute solutions you cannot avoid, you know considering the osmotic pressure because the osmotic pressure is based on the  $c_s$ , surface concentration which is going to be much higher than the feed solute concentration  $c_1$ , okay.

So this concentration is often much greater than the bulk concentration  $c_1$  especially permeate flux is high and then solute diffusivity is low. And then concentration just inside the pores, let us assume it is  $c_m$ , pictorially we are representing, going to represent.  $c_s$  is the surface concentration here. Just let us say the pore you know is starting here, so right at this point, right at this point at the just inside the pore the concentration of the solute is again going to be different from  $c_s$  and  $c_1$ , okay. What is that? We do not know.

Let us assume it is  $c_m$ . And then surface concentration is  $c_s$  which is much more higher than the feed concentration  $c_1$ .  $c_m$  is definitely different from the  $c_s$  but it is lower than  $c_s$  by a factor  $K$  which is known as the equilibrium partition coefficient, right. Such kind of similar discontinuity would be there for the solute concentration where selective layer joins the large pore support in general. So pictorially if you see this concentration variation or concentration gradient for ultra-filtration membrane, so this is the kind of membrane surface towards the support and this is, this line is a kind of, you know membrane surface exposed to the feed solution which is going to be separated, right.

So now this is the selective layer thickness. We do not know what it is, okay; we do not want to know as of now. It is  $L$ . And the support is, you know, thickness of the support is much more higher than the membrane thickness in general. So this is the support.

On this support there is a selective membrane layer is there. That is this one. And then the feed solution is flowing around the surface like this because it is a cross flow filtration. It is not dead end filtration. So the solute concentration in the feed that is in the bulk solution is  $c_1$ , right. But you know as the process moves on so then particles will be deposited on the surface, on the surface of membrane. So because of that one, you know the surface concentration or the

concentration of the solute on the surface is going to be much higher, much higher compared to the bulk concentration of the feed, because till this point there is no separation.

There is no separation or concentration change are supposed to be. But you know the solute concentration near the selective layer, on the selective layer surface is going to be very much higher because of this gel formation or because of the concentration polarization, right. That concentration we call it as  $c_s$  at the membrane surface. And let us say this is the membrane surface, right. So here on this membrane surface, on this membrane surface we have taken one particular pore.

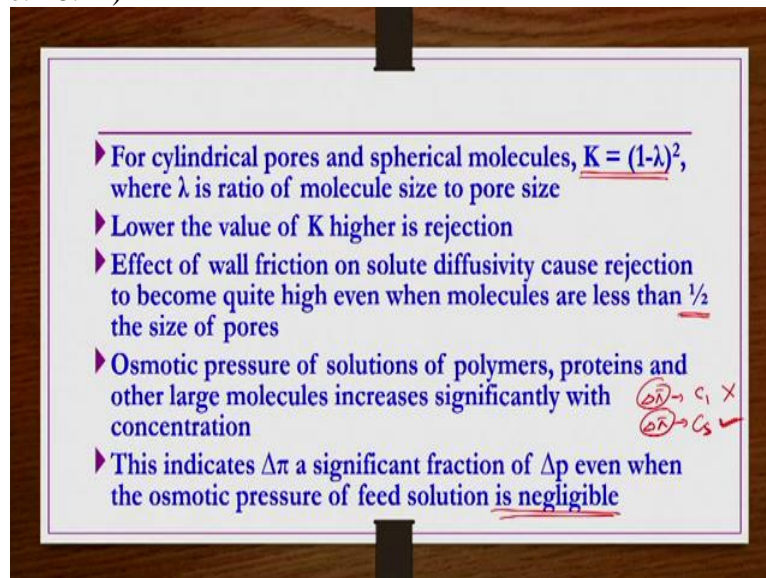
So on the surface the concentration is  $c_s$ , okay but just inside the, just inside the membrane pore, whatever the pore, one selected pore we have taken here, the concentration is  $c_m$  which is going to be less than the  $c_s$ , which is going to be less than the  $c_s$  that is  $c_m$ . But it is definitely going to be more than the  $c_1$ , more than the  $c_1$ . So this the level,  $c_1$  is at lower level,  $c_s$  is at the higher level,  $c_m$  is the, you know between these two but towards the  $c_1$ , okay. And then towards the permeate you know once this whatever the solution passes through here, so some solutes will also be passing through.

So then from here the permeate is collected. So permeate is in general, you know, pure, almost pure but not completely pure. So there will be some solute particles. So then solute concentration in the permeate side is  $c_2$ . So pictorially if you represent concentration polarization this is what you get. So now here what we can say, the concentration from the bulk, you know it is almost stable to certain distance, almost constant to certain distance but after that it is gradually increasing and then increasing to the such high concentration  $c_s$  at the surface, right.

So now we can separate the distance in two parts towards the membrane. So towards the bulk flow, bulk fluid side, whatever the distance is there, you just leave it as it is. Let us say this point, from here the concentration gradually increases and then it increases to such large concentration as  $c_s$  at the membrane surface. So this distance, this distance you take it as a kind of delta, okay. Looks like  $\delta$  here but it is a kind of a delta. So this distance what we do, you take as a kind of delta. So at  $x$  is equals to 0, the membrane surface, at  $x$  is equals to 0 what is the concentration?

Here is  $c_s$ , at  $x$  is equals to  $\Delta$  onwards and towards the bulk side, what is the concentration? It is nothing but  $c_1$ . These are the boundary conditions. So now some changes, concentration change with respect to distance is happening only from  $x$  is equals to 0 to  $x$  is equals to  $\Delta$ . So what is that function we have to find out if we wanted to find out what is  $c_s$ , okay? So that is what we are going to do in here.

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Now in general for cylindrical pores and then spherical molecules whatever the partition coefficient  $K$  is there, that is given as you know  $(1 - \lambda)^2$  where the  $\lambda$  is the ratio of molecule size to the pore size. Lower the value of  $K$  higher is the rejection in general. But however effect of wall friction on solute diffusivity also cause the rejection to become quite high even when the molecules are less than the half the pore size, that is even when  $\lambda$  is less than half, you know what happens there is a kind of wall friction on solute diffusivity.

Effect of wall friction on solute diffusivity is there. That makes this rejection very high even when this  $\lambda$  value is less than  $1/2$ . Further osmotic pressure of solutions of polymers, proteins and other large molecules increases significantly with the concentration. So osmotic pressure if you calculate based on the  $c_1$  that is feed concentration, that is not going to give correct thing because this  $\Delta\pi$  in general increases for any of these polymer solutions, protein solutions etc with increase in the concentration.

So at the surface, the concentration  $c_s$  is much higher than the  $c_1$  so whatever the osmotic pressure using the  $c_s$  concentration, that is going to be the correct one, okay. This indicates, what we indicate that you know,  $\Delta\pi$ , a significant fraction of  $\Delta p$  should be considered even when the osmotic pressure of feed solution is negligible, even if osmotic pressure of feed solution is negligible because  $c_1$  is very, very small in general.

Despite of that one,  $\Delta\pi$  has to be incorporated in this equation because what happened, in the ultrafiltration membrane because of the concentration polarization, surface concentration gradually increases, and then it reaches certain maximum concentration for a given thickness of the feed layer, okay. At that maximum concentration  $c_s$ , this osmotic pressure is going to be much higher compared to the osmotic pressure calculated based on the feed concentration. So because of that reason even if the feed solution osmotic pressure is negligible, the has to be incorporated in the equation.

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▶ In RO, concentration polarization is treated using simple mass transfer equation, i.e., equating the diffusion flux to amount of solute rejected per unit membrane area, is satisfactory where surface concentration is only moderately higher than that of bulk  
 ▶ For UF, large change in concentration near the surface requires integration to obtain concentration profile  
 ▶ Balance eq.: flux of solute due to the convection + diffusion is constant in the boundary layer and equal to the flux of solute in the permeate:  $vc + D_v \frac{dc}{dx} = vc_2 \Rightarrow (5)$   
 ▶ Boundary conditions:  $c = c_s$  at  $x = 0$  and  $c = c_1$  at  $x = \delta$

But on the other hand in general in reverse osmosis concentration polarization is treated using simple mass transfer equation that is equating the diffusion flux to amount of solute rejected per unit membrane area. That is itself is satisfactory where surface concentration is only moderately higher than that of bulk, like in reverse osmosis also such kind of concentration polarization would be there.

But there we do not need to worry about you know variation of concentration with respect to the x distance, from x is equals to 0 to  $\delta$  because the  $c_s$  and  $c_1$  variation is in general very, very

small in the case of a reverse osmosis. Like  $c_s - c_1$  is very small, that can be in general neglected in the case of reverse osmosis so then you do not need to find out how this  $c_s$  is changing from  $c_s$  to  $c_1$  as  $x$  is increasing from  $x$  is equals to 0 to  $x$  is equals to  $\delta$ , that you do not need to do in case of reverse osmosis because that difference is very small.

But in ultra-filtration that is going to be very significant one. So we cannot avoid that, you know variation, whatever the concentration variations with  $x$  direction near the surface we cannot avoid in ultra-filtration. So that is what we are going to do now. So for ultra-filtration, large change in concentration near the surface requires integration to obtain concentration profile. So if you want to integrate you have to develop a kind of differential equation. That you can get by doing the basic balance equation.

So what kind of balance that we can have near the surface, membrane surface? Flux of solute due to convection plus diffusion is constant in the boundary layer and it is equals to the flux of the solute in the permeate. So let us say if I redraw, this is the kind of membrane surface, this is a kind of support and then here we have a kind of permeate of concentration  $c_2$ . So on the surface here the  $c_s$  concentration is there. And then at the bulk  $c_1$  is there, so in this distance  $x$  is equals to 0 to  $x$  is equals to  $\delta$  the concentration is changing from  $c_s$  to  $c_1$ .

So this variation whatever is there, that you know we have to take care and then where the convection and diffusion both are taking place, so whatever the near the surface that is in the boundary layer, this boundary layer  $\delta$  so within this boundary layer whatever the flux, solute flux is there because of the convection and diffusion that should be equal to the flux of the same solute in the permeate, okay. That will give you the basic flux balance at the membrane surface.

So in the boundary layer the solute flux due to the convection is  $vc$  and then in the boundary layer the solute flux due to the diffusion is  $D_v \frac{dc}{dx}$ . Let us take  $D_v$  as a kind of diffusivity and then solute flux in the permeate side is  $vc_2$ . And then what are the boundary conditions? At  $x$  is equals to 0 that is on the membrane surface  $c$  is equal to  $c_s$  and  $x$  is equals to  $\delta$  that is the outermost layer of the, boundary layer whatever the concentration polarization because of the concentration polarization whatever the boundary layer is formed that thickness is  $\delta$ .

So outer layer of that, I know the boundary layer is exposing towards the bulk fluid, so the concentration should be  $c_1$ . So from this point onwards you know concentration is everywhere. Here it is  $c_1$ , okay. So now this equation you solve and then apply these boundary conditions so then you will be having expression to get  $c_s$  as function of  $c_2$ . That is what we are going to do now.

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$$vc + D_v \frac{dc}{dx} = vc_2 \Rightarrow v(c - c_2) = -D_v \frac{dc}{dx}$$

$$\Rightarrow \frac{v}{D_v} dx = -\frac{dc}{(c - c_2)} \Rightarrow \frac{v}{D_v} x \Big|_0^\delta = -\ln(c - c_2) \Big|_{c_s}^{c_1}$$

$$\Rightarrow \frac{v}{D_v} \delta = \ln \left( \frac{c_s - c_2}{c_1 - c_2} \right)$$

$$\Rightarrow \ln \left( \frac{c_s - c_2}{c_1 - c_2} \right) = \frac{v}{D_v} \delta = \frac{v}{k_c} \Rightarrow (6)$$

•  $D_v/\delta$  has units of length per time and is defined as the mass transfer coefficient  $k_c$

So  $vc + D_v \frac{dc}{dx} = vc_2$  that we have done just now flux balance equation at the membrane surface. So then now  $v$  terms we keep one side, other terms we take to the the remaining right side, right.

Now we can rearrange this equation  $\frac{v}{D_v} dx = -\frac{dc}{(c - c_2)}$ . When you integrate either side so  $dx$  is, integration of  $dx$  is  $x$  and then  $x$  is varying from 0 to  $\delta$ , that is within the boundary layer, okay, due to the concentration polarization whatever the boundary layer is there, that the thickness is  $\delta$  and then that is varying between 0 to  $\delta$  from membrane surface towards the feed side, ok bulk solution side. And then  $-\frac{dc}{(c - c_2)}$  is nothing, when you integrate you will get  $-\ln(c - c_2)$  and then surface concentration at  $x$  is equals to 0, concentration is  $c_s$ .

At  $x$  is equal to  $\delta$  concentration is nothing but the bulk concentration  $c_1$ . So when you apply these boundary conditions, limiting conditions we have  $\frac{v}{D_v} \delta = \ln \left( \frac{c_s - c_2}{c_1 - c_2} \right)$ . So this is the equation. Now here if you know the diffusivity and then thickness, boundary layer thickness



then you can know the  $c_s$  because  $c_1, c_2$  are known. The feed solution concentration you know and then permeate solute concentration also you know while doing the experiment. So  $c_s$  you can know from here.

The same equation if you rearrange this what  $\frac{D_v}{\delta}$  is having a kind of meter per second units, so that is we can call it as kind of a mass transfer coefficient  $k_c$ . So  $\ln\left(\frac{c_s - c_2}{c_1 - c_2}\right)$  we can write by, we can write it as  $\frac{v}{k_c}$ .  $\frac{D_v}{\delta}$  has units of length per unit and is defined as the mass transfer coefficient  $k_c$ , okay. This is the case when the rejection is partial. Indeed, in reality most of the cases, the partial rejection only takes place. Complete rejection never takes place; very rarely it takes place, right. So in case if you have a kind of a complete rejection then  $c_2$  should be 0 in the same equation. Then  $\ln\frac{c_s}{c_1}$  should be equal to  $\frac{v}{k_c}$ .

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• For simple case of complete solute rejection,  $c_2 = 0$  and above eqn. reduces to:  $\ln\left(\frac{c_s - c_2}{c_1 - c_2}\right) = \frac{v}{k_c} \Rightarrow v = k_c \ln\left(\frac{c_s}{c_1}\right) \Rightarrow (7)$

• Permeate flux is a nonlinear function of  $\Delta p$  due to concentration polarization, and a trial and error solution is needed to calculate  $v$  for a given  $\Delta p$

• However, when there is a complete rejection of solute and no gel resistance,

- $\Delta p$  for a specified  $v$  can be obtained directly by using eqn. (7) to get  $c_s$  and osmotic pressure data to get  $\Delta\pi$  (is function of concentration), which is added to term  $(\Delta p - \Delta\pi)$  from eqn. (3) to give  $\Delta p$   $v = \frac{\Delta p - \Delta\pi}{R_m + R_{gel}} \Rightarrow (3)$

For simple case of complete solute rejection which is not possible in general, however if you have a case where complete rejection is taking place then  $c_2$  is equals to 0 and then in above equation  $\ln\left(\frac{c_s - c_2}{c_1 - c_2}\right) = \frac{v}{k_c}$ . If you substitute  $c_2$  is equals to 0 then we have  $v = k_c \ln\frac{c_s}{c_1}$ , okay.

So now what we understand further, permeate flux is non-linear function of  $\Delta p$  due to this concentration polarization and trial and error solution is needed to calculate  $v$  for a given  $\Delta p$ . Actually if it is pure water then you know water flux you know linearly increases with the  $\Delta p$ .

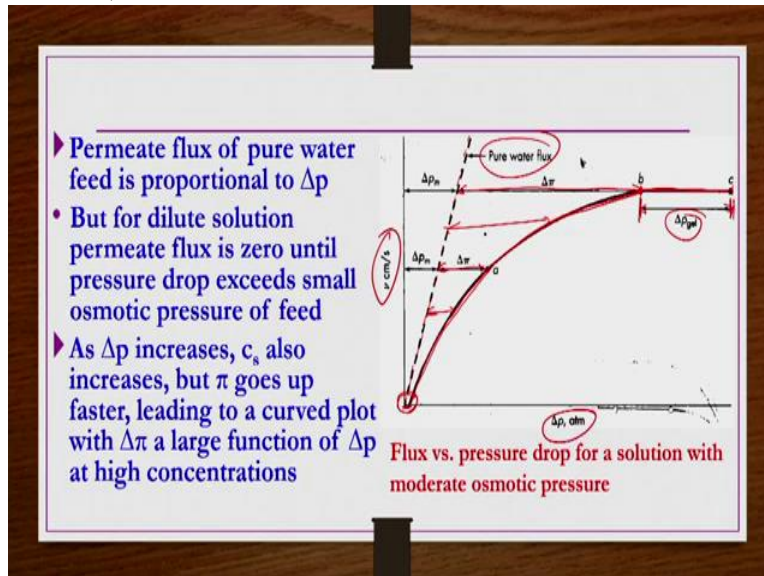
If you have a dilute solution which you wanted to purify by some membranes, by using membranes in this ultrafiltration then that flux of the solution, you know it is non-linear. It is non-linear, okay.

We are going to see that one also. So however when there is complete rejection of solute and no gel resistance is there,  $\Delta p$  for specified  $v$  can be obtained directly by using equation 7. From here you can get the  $c_s$  and then once you know the  $c_s$  you can know the  $\Delta\pi$  and once you know the  $\Delta\pi$ , so then we can use this equation to get  $\Delta p$  for a required  $v$ .

Basically what this statement says that, let us say if you wanted to have 0.0001 L/m<sup>2</sup>h of permeate flux how much  $\Delta p$  should you apply? That is what you wanted to calculate, okay. So then for that you need to know  $\Delta\pi$  also. How much  $\Delta p$  is required, if you want to calculate how much  $\Delta p$  is required for a specified permeate flux, let us say 0.001 L/m<sup>2</sup>h of permeate flux, if you want to obtain by using ultra-filtration membrane then how much  $\Delta p$  should you apply. That you can calculate by these equations.

For that you need  $\Delta\pi$ . So this  $\Delta\pi$  can be obtained by the  $c_s$  concentration. And  $c_s$  you can obtain from the equation number 6 or 7 depending on the rejection. If the complete rejection then equation number 7 can be used, if partial rejection then equation number 6 can be used; that is the point of using this equation. So this developed equation is used in 2 ways. You can directly, you know obtain what is the surface concentration or the solute concentration at the surface  $c_s$  or you can obtain you know  $\Delta p$  required to maintain the specified permeate flux. Either way you can use these equations.

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Now let us say, as I mentioned already you know, whatever the flux is there if it is for the pure water it is going to be linear in general. So then, but if you have a kind of a solution, if you have a kind of dilute solution and then using the membrane for separating that solution so that you can have a kind of clear permeate and then concentrated retentate as a kind of separate layer.

Then this flux is not going to be linear with  $\Delta p$ , why? Because there is a kind of osmotic pressure because of these solute particles, right. Because of that osmotic pressure even if you apply certain pressure initially so for initial certain  $\Delta p$  there will not be any kind of flux. Now here you can see at the origin this pure water flux is passing through the origin. But the other line, the solid line is a kind of, you know permeate flux for a kind of a solution.

We need to take a dilute solution then the flux would be having like this and then this is not passing through origin. That means the solute, you know, retention will be there. And then permeate flux will only start after certain  $\Delta p$  has to be applied and that  $\Delta p$  is nothing but you know, that is osmotic pressure has to be overcome then only flux, permeate flux will start coming out, okay the permeate will start coming through the membrane.

Until that pressure, until and unless that pressure is crossing that osmotic pressure the separation will not take place. So this, this is the region, here it is not passing through the origin. So permeate flux of pure water feed is proportional to  $\Delta p$  and then you can see this

proportionality, kind of linear plot you can see here, okay. So this is increasing with increase in the  $\Delta p$  linearly.

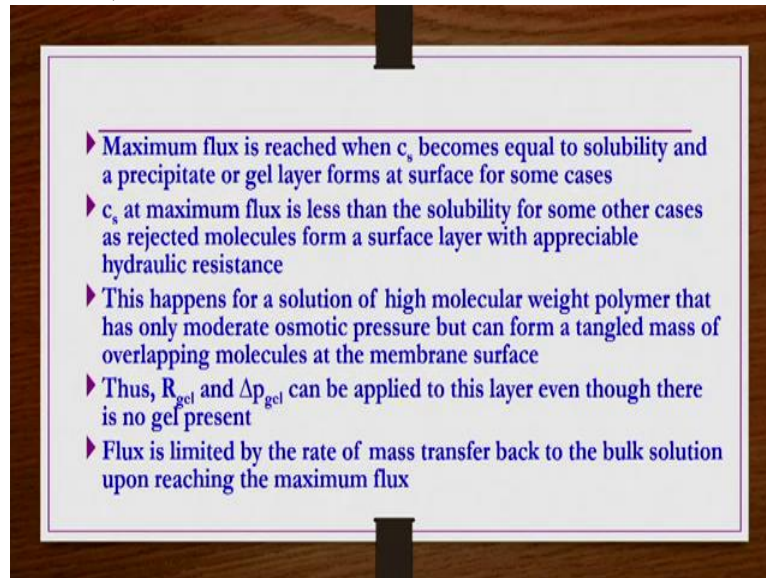
But for dilute solution, permeate flux is 0 until pressure drop exceeds small osmotic pressure, whatever small osmotic pressure is there because of the presence of solutes in the solution, you know there is a small osmotic pressure. Until and unless the applied pressure exceeds that osmotic pressure the permeate flux will not be there, it will be 0, okay. Then after that, you know after crossing this osmotic pressure, further if you increase this pressure, when you start applying the pressure, gradually you increase the pressure, right.

So there will be a kind of pressure drop which is equal to the osmotic pressure and after that permeate is started coming. But after that osmotic pressure if you further increase the applied pressure then what happens? Let us say 1.1 is a kind of, 1.1 atmosphere is a kind of osmotic pressure for a given solution. Then up to 1.1 pressure drop there will not be any permeate and permeate will be 0. And after 1.1 atmosphere, you further gradually increase the pressure drop, the flux is going to increase gradually but this increase is a kind of non-linear like this and then after certain point let us say, from this b to c point it is going to be constant. That is the point where the gel formation is there and gel is offering a lot resistance.

That resistance is known as the  $\Delta p_{gel}$  which is not allowing further flux increase. With increase in  $\Delta p$ ,  $c_s$  increases, right.  $c_s$ , that is the concentration, solute concentration on surface increases because more and more particle would be you know forming or contributing towards the gel formation. So  $c_s$  concentration would increase. But  $c_s$  concentration may be slightly increasing but the corresponding osmotic pressure you can see, it is largely increasing. How largely it is increasing from one level to the other level gradually you can see.

So this is called  $\Delta\pi$ . So as the pressure drop increases, the osmotic pressure is increasing to the larger extent; faster, faster rate increases. This is the permeate flux versus pressure drop plot for a kind of ultrafiltration membrane. In general this is what you find, okay.

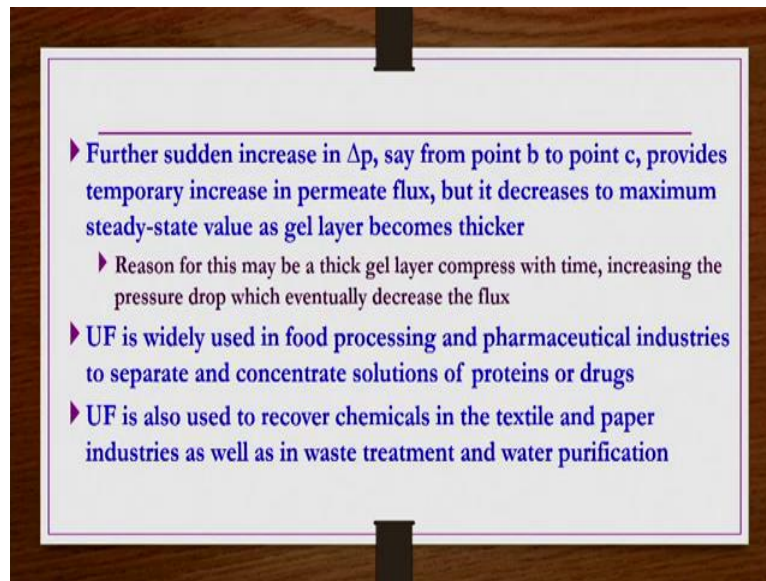
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This maximum flux whatever is there, that is reached when  $c_s$  becomes equal to the solubility and precipitate or gel layer forms at surface for some cases. But however in some cases  $c_s$ , if maximum flux is less than the solubility, as the rejected molecules form the surface layer with appropriate hydraulic resistance which is, because you know, whatever the particles are there, tangled mass of overlapping molecules at the membrane surface, they cause a kind of increased rejections for these kind of cases where the maximum flux is attained and then  $c_s$  is less than the solubility. Despite of that one also rejection increases.

So now what we understand here? So whether the gel formation is there or not,  $R_{gel}$  and  $\Delta p_{gel}$  can be applied to this layer even when there is no gel present because the gel formation is going to take place gradually with increase in the  $\Delta p$ . So flux is limited by the rate of mass transfer back to the bulk diffusion upon reaching the maximum flux. After this point whatever the flux is there, here it is controlled by the mass transfer, okay.

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Further sudden increase in  $\Delta p$ , say from that point b to c in the picture we have seen, in the picture we have seen, that provides a temporary increase in permeate flux but it decreases to maximum steady state value as gel layer becomes thicker because you know thick gel layer compresses with time and increasing the pressure drop would eventually decrease the flux only. So this is about the, you know concentration polarization and permeate flux for the ultra-filtration membrane and then how the permeate flux is changing with the pressure drop et cetera, those kind of things we have seen about the ultra-filtration membrane.

So in general these ultra-filtration membranes are used widely in food processing and pharmaceutical industries to separate and concentrate solutions of proteins or drugs. UF is also used to recover chemicals in the textile and paper industries as well as in waste treatment and water purifications. We have seen a few specific applications in the previous lecture and then some generalized applications are given here for ultra-filtration membranes.

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**Example - 1**

- A tubular membrane with a diameter of 2cm and a water permeability of 250 l/m<sup>2</sup>.h.atm is being used for UF of cheese whey at room temperature. The whey proteins have an average diffusivity of 4×10<sup>-7</sup> cm<sup>2</sup>/s; and the osmotic pressure (in atmospheres) is given by  $\pi = 4.4 \times 10^{-3} \times (c) - 1.7 \times 10^{-6} \times c^2 + 7.9 \times 10^{-8} \times c^3$ ; where C is the protein concentration in grams per liter. The mass transfer is described by  $Sh = 0.0096Re^{0.913}Sc^{0.346}$ .
- For the conditions of protein concentration 10g/L, solution velocity 1.5m/s, gel concentration 300g/L and 100% rejection, what is the permeate flux and what  $\Delta p$  should be applied to achieve this permeate flux? Assume bulk solutions have the same density and viscosity as of water at room temperature.

Now what we do? Based on this you know permeate flux and then concentration polarization concept for ultra-filtration membrane whatever we have seen, we try to solve couple of problems. A tubular membrane with a diameter of 2 centimeter and water permeability of 250L/m<sup>2</sup>h.atm. is being used for ultra filtration of cheese whey at room temperature. The whey proteins have an average diffusivity of 4 x 10<sup>-7</sup> cm<sup>2</sup>/s and osmotic pressure is given by this equation where C is the protein concentration in g/L.

The mass transfer is described by the Sherwood number and Sherwood number as function of Reynolds number and Schmidt number is given here. So now for the conditions of protein concentration, protein concentration 10 g/L that is the  $c_1$  is given, and then solution velocity 1.5 meter per second and gel concentration that is  $c_s$  is given, 300 gram per liter.  $c_1$  is 10 g/L so now you can see  $c_s$  is 300 g/L, 30 times higher, okay. And 100% rejection is there.

So under such condition what is the permeate flux and what  $\Delta p$  should be applied to achieve this permeate flux? So we need some kind of properties such as density and viscosity. So for that bulk solutions have the same density and viscosity as of water at room temperature, that we can assume as per the problem statement, okay. So we need to find out what is permeate flux and then what is pressure drop to maintain this permeate flux under 100 percent rejection conditions, right?

So  $c_s$ , we have this  $\frac{v}{k_c} = \ln\left(\frac{c_s}{c_2}\right)$ . From here we can find out the, you know this  $v$ . But  $k_c$  we have to find out. How to find out the  $k_c$ ?  $k_c$  we can find out from this Sherwood number expression. So  $Re$  you can calculate because the solution velocity is given. Density and viscosity of the fluid is given, same as the water. Schmidt number also you can calculate, so then Sherwood number you can calculate, from Sherwood number you can calculate the  $k_c$  value. Once  $k_c$  is known, from this equation you can calculate the  $v$  because  $c_s$  is also given. And then  $c_2$  is 0. This is  $\ln\left(\frac{c_s}{c_2}\right)$ .

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$D = 2\text{cm}, \bar{v} = 150 \frac{\text{cm}}{\text{s}};$   
 • At  $20^\circ\text{C}$ , water properties:  $\rho = 1\text{g/cc}, \mu = 0.01\text{g/cm.s}$   
 $Re = \frac{D\bar{v}\rho}{\mu} = \frac{2 \times 150 \times 1}{0.01} = 30,000$   
 $Sc = \frac{\mu}{\rho D_0} = \frac{0.01}{1 \times 4 \times 10^{-7}} = 25,000$   
 $Sh = 0.0096 Re^{0.913} Sc^{0.346} = 3.9 \times 10^3 = \frac{k_c D}{D_0}$   
 $\Rightarrow k_c = \frac{3.9 \times 10^3 \times 4 \times 10^{-7}}{2} = 7.8 \times 10^{-4} \text{ cm/s}$

So  $D$  is 2 cm.  $\bar{v}$  is 150 cm/s. This  $\bar{v}$  is not the permeate flux. It is the velocity. It is the velocity of the fluid that is given for the condition of protein concentration 10 g/L; solution velocity is 1.5 m/s at that whatever the across the membrane surface, feed is coming at high velocity rate. That high velocity is nothing but 1.5 m/s. It is not the permeate flux, okay. So 1.5 meter per second, I will write 150 cm/s because we will be solving this problem in CGS units.

At 20 degree Centigrade water has the 1 g/cc,  $\mu$  and 0.01 g/cm.s viscosity. So  $Re = \frac{D\bar{v}\rho}{\mu}$ ,  $D$  is 2,  $\bar{v}$  is 150,  $\rho$  is 1,  $\mu$  is 0.01 so  $Re$  is coming out as 30000.  $Sc = \frac{\mu}{\rho D_0}$  so which is given as a kind of, you know,  $\mu$  is given as 0.01,  $D_0$  is  $4 \times 10^{-7}$  and then  $\rho$  is 1. All are in CGS units.



So it is coming 25000. So the Sherwood number, it is given as like this in the problem, so in the Sherwood number expression, you substitute Schmidt number and Reynolds number, so you will get Sherwood number is  $3.9 \times 10^3$  which is, definition of Sherwood number is nothing but  $\frac{k_c D}{D_0}$  is the diffusivity. So now from here you can find out the  $k_c$ .  $k_c$  is equals to  $3.9 \times 10^3$  into diffusivity is  $\frac{4 \times 10^2}{2}$  is the diameter. Then you will get  $k_c$  you will get it as  $7.8 \times 10^{-4}$  cm/s.

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• Permeability,  $Q_m = 250 \text{ l/m}^2 \cdot \text{h} \cdot \text{atm} = 6.94 \times 10^{-3} \text{ cm/s} \cdot \text{atm}$   
 •  $v = Q_m \Delta p = Q_m (\Delta p - \Delta \pi) \Rightarrow \Delta p - \Delta \pi = \frac{v}{Q_m} = \frac{v}{6.94 \times 10^{-3}}$   
 • Since rejection is 100%  $\Rightarrow \frac{v}{k_c} = \ln \frac{c_2}{c_1}$   
 $\Rightarrow v = 7.8 \times 10^{-4} \times \ln \left( \frac{300}{10} \right) = 2.653 \times 10^{-3} \frac{\text{cm}}{\text{s}}$   
 • Osmotic pressure:  
 $\Delta \pi = \pi = 4.4 \times 10^{-3} \times (300) - 1.7 \times 10^{-6} \times 300^2 + 7.9 \times 10^{-8} \times 300^3$   
 $= 3.3 \text{ atm}$   
 • Pressure drop:  $\Rightarrow \Delta p - \Delta \pi = \frac{v}{Q_m} = \frac{v}{6.94 \times 10^{-3}} \Rightarrow \Delta p = 3.3 + \frac{2.653 \times 10^{-3}}{6.94 \times 10^{-3}} = 3.682 \text{ atm}$

So permeability,  $Q_m$  is given as  $250 \text{ L/m}^2 \cdot \text{h} \cdot \text{atm}$ , so that we have to convert into the cm/s, so then you will get this one. And then  $v = Q_m \Delta p = Q_m (\Delta p - \Delta \pi)$  we have to have because now it is a dilute solution, dilute cheese whey solution so  $(\Delta p - \Delta \pi)$  should be  $\frac{v}{Q_m}$ .

So  $v$  is the, you know whatever the permeate is there, that we have to find out and then  $Q_m$  is the permeability that is  $6.9 \times 10^{-3}$ , that is again given, okay. So now in this equation if you wanted to find out  $v$  you need to find out  $\Delta \pi$ . You need to find out  $\Delta p$  also, okay. But for 100% rejection case we know that  $v = k_c \ln \left( \frac{c_2}{c_1} \right)$ . So we do not need to find out  $v$  from here, we can find out from here because it is given in the problem statement for 100 percent rejection conditions.

So from here  $v$  you will get,  $k_c$  that is  $7.8 \times 10^{-4}$  cm/s,  $\ln c_2$  is 300 gram per liter,  $c_1$  is 100 gram per liter given in the problem. So then you will have this  $2.653 \times 10^{-3}$  cm/s as a kind of permeate

flux. So permeate flux is known. So now  $v$  is also known from here. So now you need to find out what is  $\Delta p$ . For that you just need to find out  $\Delta\pi$ .

$\Delta\pi$  osmotic pressure expression is also given. In place of  $c$  you have to substitute  $c_s$  values because we wanted to know the osmotic pressure, you know at the membrane surface. At the membrane surface the concentration is  $c_s$ . So 300 when you substitute here in this osmotic pressure equation which is given then you will get osmotic pressure as 3.3 atmosphere. So  $\Delta p - \Delta\pi = \frac{v}{Q_m}$ . Then  $v$  is already  $2.65 \times 10^{-3}$  that we have calculated.

Permeability  $Q_m$  is given as  $6.94 \times 10^{-3}$ . Osmotic pressure you just calculated as 3.3, so 3.683 atmosphere of pressure drop you should apply if you wanted to have a kind of 100% rejection with permeate flux,  $2.65 \times 10^{-3}$  cm/s, okay.

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**Example - 2**

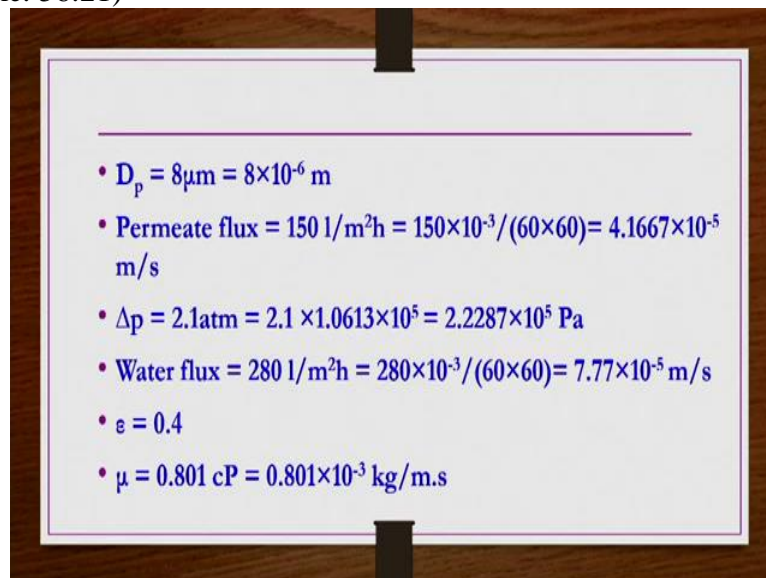
- A membrane filtration process is used to concentrate a suspension of  $8 \mu\text{m}$  spherical particles, has a permeate flux  $150 \text{ L/m}^2\text{h}$  at  $30^\circ\text{C}$  and a pressure drop of  $2.1 \text{ atm}$ . Under the same conditions, the pure water flux is  $280 \text{ L/m}^2\text{h}$ .
- Calculate the resistances of the membrane and the gel layer.
- How thick a layer of particles would be needed to account for the gel-layer resistance if  $\varepsilon = 0.4$  and  $\mu = 0.801 \text{ cP}$ .

We take another example problem. A membrane filtration process is used to concentrate a suspension of  $8 \mu\text{m}$  spherical particles, has a permeate flux of  $150 \text{ L/m}^2\text{h}$  at  $30$  degree Centigrade and the pressure drop of  $2.1$  atmosphere. Under the same condition the water flux is  $280 \text{ L/m}^2\text{h}$ . Calculate the resistance of the membrane and the gel layer, that is  $R_m$  and then  $R_{gel}$  we have to find out. In addition we have to find out how thick a layer of particles would be needed to account for the gel layer resistance if  $\varepsilon$  is  $0.4$  and then  $\mu$  is  $0.801 \text{ cP}$  that is  $L$  we have to find out.

That is L is like you know, on the membrane you know this is the membrane, okay. On this membrane the particles, gel layers are formed. The particles are forming a kind of gel layers, right. What is thickness of this gel layer L? This we have to find out. So for this we can use the Kozeny Carman equation that kind of form that  $\frac{\Delta p}{L}$  equals to, from the Kozeny Carman equation we have that  $\frac{\Delta p}{L} = \frac{150\mu v(1-\epsilon)^2}{\phi_s^2 D_p^2 \epsilon^3}$ .

That expression we can use, right. In that expression  $\Delta p$  is known, only L that we can know. L is nothing but the length of the packing. Now here that length of the or the thickness of the gel whatever is there, that is L here in this case. Okay, so before that we have to find  $R_m$  and  $R_{gel}$ . Let us see that one.

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- $D_p = 8\mu\text{m} = 8 \times 10^{-6} \text{ m}$
- Permeate flux =  $150 \text{ l/m}^2\text{h} = 150 \times 10^{-3} / (60 \times 60) = 4.1667 \times 10^{-5} \text{ m/s}$
- $\Delta p = 2.1 \text{ atm} = 2.1 \times 1.0613 \times 10^5 = 2.2287 \times 10^5 \text{ Pa}$
- Water flux =  $280 \text{ l/m}^2\text{h} = 280 \times 10^{-3} / (60 \times 60) = 7.77 \times 10^{-5} \text{ m/s}$
- $\epsilon = 0.4$
- $\mu = 0.801 \text{ cP} = 0.801 \times 10^{-3} \text{ kg/m.s}$

$D_p$  is given, permeate flux is given so we converted in meter per second,  $\Delta p$  is given, it is converted into the Pascal. Water flux is also given in  $\text{L/m}^2\text{h}$ . If you convert into the  $\text{m/s}$  units it comes like this.  $\epsilon$  is given,  $\mu$  is given, okay. So in  $\text{kg/m.s}$  it is  $0.801 \times 10^{-3}$ .

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• Pure water flux =  $\Delta p / R_m \rightarrow R_m = (2.2287 \times 10^5) / (7.777 \times 10^{-5}) = 2.866 \times 10^9 \text{ m}^{-1}$   
 • For solution by UF:  $v = \frac{\Delta p - \Delta \pi}{R_m + R_{gel}} \Rightarrow 4.1667 \times 10^{-5} = \frac{2.2287 \times 10^5 - 0}{2.866 \times 10^9 + R_{gel}} \Rightarrow R_{gel} = 2.484 \times 10^9 \text{ m}^{-1} *$   
 •  $\Delta p = \Delta p_{gel} + \Delta p_{memb} = 2.1 \text{ atm}$   
 • Since  $\Delta p \propto \text{flux} \rightarrow \Delta p_{memb} = 2.1 \times 150 / 280 = 1.125 \text{ atm}$   
 • Thus,  $\Delta p_{gel} = 2.1 - 1.125 = 0.975 \text{ atm} = 9.88 \times 10^4 \text{ Pa}$

So the pure water flux is nothing but  $\frac{\Delta p}{R_m}$ . Right, so from here  $\Delta p$  is given so  $R_m$  should be  $\Delta p$  by pure water flux. Pure water flux is also given. So  $\Delta p$  is nothing but, we converted in Pascal so it is 2.1 atmosphere but in Pascal it is  $2.2287 \times 10^5$  Pascals divided by the permeate flux is given in pure water, it is pure water so pure water flux is given in  $\text{L/m}^2\text{h}$ . In meter per second if you convert it comes out to be  $7.77 \times 10^{-5}$ .

So  $R_m$  comes out to be  $2.866 \times 10^9 \text{ m}^{-1}$ , straight forward. So similarly for solution this equation we know permeate flux is nothing but  $\frac{\Delta p - \Delta \pi}{R_m + R_{gel}}$ . So permeate flux is also given  $150 \text{ L/m}^2\text{h}$ , so that we converted into m/s like this. Now  $\Delta p$  it is given 2.1 atmosphere, in Pascals it is  $2.2287 \times 10^5$  Pascals minus  $\Delta \pi$  we can take it as 0 because it is first of all the solute concentration is not given, so we assume that the solute concentration is very, very small.

So then we can take it as a kind of 0. So then from here,  $R_m$  is also known. So from here  $R_{gel}$  we can find it out. So  $R_{gel}$  is equals to  $2.484 \times 10^9 \text{ m}^{-1}$ . What we can see here, the gel resistance is not small compared to the membrane resistance. Indeed both of them are almost equal. So whatever the membrane resistance the same amount of resistance is, almost same amount of resistance is also offered by the gel. So gel layer one cannot avoid easily otherwise results may be going wrong.

So gel layer resistance is also very significant in ultra-filtration. So  $\Delta p$  overall is 2.1 atmosphere but that should be  $\Delta p_{gel} + \Delta p_{membrane}$ , whatever the resistance offered by the membrane and

whatever the resistance offered by the gel are there, so across these 2 layers whatever the pressure drops are there they would be added together to get the total pressure drop as same as in cake filtration we have done, right.

So now, but you know  $\Delta p$  is proportional to the flux, is not it? So then delta p membrane you can find it out,  $2.1 \times 150/280$ , 150 is the permeate flux, 280 is the pure water flux so from here  $\Delta p_{membrane}$  you will get 1.125 atm. So then  $\Delta p_{gel}$  you can get it as  $(2.1 - 1.125)$  so that is 0.975 atm which is  $9.88 \times 10^4$  Pascals, right.

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• We have,  $\frac{\Delta p}{L} = \frac{150\mu v(1-\varepsilon)^2}{\phi_s^2 D_p^2 \varepsilon^3} =$   
 $\frac{150 \times 8.01 \times 10^{-4} \times 4.1667 \times 10^{-5} \times 0.6 \times 0.6}{1 \times (8 \times 10^{-6}) \times (8 \times 10^{-6}) \times 0.4^3} = 4.4 \times 10^5 \text{ Pa/m}$   
 $\rightarrow L = (9.88 \times 10^4) / (4.4 \times 10^5) = 0.224\text{m}$

Then we have to find out this layer of particles, whatever the gel layer has formed so that is having some thickness that we have to find out. So as I mentioned so if this is membrane, on the surface the particles are forming. So this layer, though it is very thin, so we can apply the principles of flow through packed bed and then we can use this Kozeny Carman equation that is  $\frac{\Delta p}{L} = \frac{150\mu v(1-\varepsilon)^2}{\phi_s^2 D_p^2 \varepsilon^3}$ . Here except L everything is known. So what we do?  $\frac{\Delta p}{L}$ , right hand side when you calculate you will, after substituting all these values you will get  $4.4 \times 10^5$  Pascal per meter, right. Now  $\Delta p$  is also known.

So L should be  $\Delta p$  divided by whatever this  $4.4 \times 10^5$  is there, that when you do you will get L as 0.224 meters. So 0.224 meters thick particles are formed as a kind of gel layer. So gel layer thickness is nothing but 0.224 meters. It is very significant one.

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**Partial rejection of solutes**

- ▶ Membrane selected has some pores that are larger than solute molecules in many UF applications, thus solute is rejected partially only
- ▶ Fraction rejected  $R$  is sometimes defined using feed and permeate concentrations as:  
$$R_F \equiv 1 - \frac{c_p}{c_f} \Rightarrow (8)$$
- ▶ But concentration changes along the length of a separator, a more fundamental definition of  $R$  based on local retentate and permeate compositions  $C_1$  and  $C_2$  is required as given below:  
$$R \equiv 1 - \frac{c_2}{c_1} \Rightarrow (9)$$

So finally we see the partial rejection of solute. So we have seen there are 3 cases, permeate flux and then you know percentage of rejection and then solute concentration and retentate are the kind of three important things which describe the performance of the ultrafiltration membrane. So permeate flux we have seen. Now we are going to see the partial rejection of solutes. In general membranes whatever we select they have the pores which are larger than the solute molecules in many ultra-filtration applications.

So because of that one only partial rejection takes place. It is not possible to get a kind of complete rejection in general. So fraction rejected  $R$  is sometimes defined using the feed and permeate concentrations as  $R_F = 1 - \frac{c_p}{c_f}$ . But the  $c_f$  we have seen especially in ultrafiltration membrane it is very much different. It is very much different from one location to the other location, especially the boundary layer that is forming because of the concentration polarization.

The concentration varies from  $\frac{c_1}{c_s}$ . So feed concentration  $c_1$  we cannot use,  $c_s$  in general we do not know. So what happens? People in general use, you know retentate concentration. So that is  $1 - \frac{c_2}{c_1}$  is as a kind of  $R$ , rejection.  $c_2$  is nothing but the permeate concentration.  $c_1$  is nothing but the retentate concentration. Terminology is different here, okay.

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▶ R depends mainly on ratio of solute size to pore size  $\lambda$  (which determines the partition coefficient K) and on ratio  $v/k_c$  (which determines the concentration polarization effect)

▶ From eqns. 6 and 9:  $c_s = c_1 \left( 1 - R + R \cdot \exp\left(\frac{v}{k_c}\right) \right) \Rightarrow (10)$

$R \equiv 1 - \frac{c_2}{c_1} \Rightarrow (9) \Rightarrow 1 - R = \frac{c_2}{c_1} \Rightarrow c_2 = (1 - R)c_1$

$\ln\left(\frac{c_s - c_2}{c_1 - c_2}\right) = \frac{v}{D_v} \delta = \frac{v}{k_c} \Rightarrow (6) \Rightarrow \frac{c_s - c_2}{c_1 - c_2} = \exp\left(\frac{v}{k_c}\right) \Rightarrow \frac{c_s - c_2}{(1 - \frac{c_2}{c_1})c_1} = \exp\left(\frac{v}{k_c}\right)$

$\Rightarrow c_s - c_2 = c_1 R \cdot \exp\left(\frac{v}{k_c}\right) \Rightarrow c_s = c_2 + c_1 R \cdot \exp\left(\frac{v}{k_c}\right) = (1 - R)c_1 + c_1 R \cdot \exp\left(\frac{v}{k_c}\right)$

$\Rightarrow c_s = c_1 \left( 1 - R + R \cdot \exp\left(\frac{v}{k_c}\right) \right)$

So  $c_2$  is permeate concentration and  $c_1$  is the retentate concentration here, not the feed concentration, okay. And then R depends mainly on ratio of solute size to pore size which determines the partition coefficient and ratio of  $\frac{v}{k_c}$  which determines the concentration polarization effect. Both are very much important factor in ultrafiltration. So we have to bring in those factors here.

So whatever the equation number 6 to 9 we have, so if we combine then we can get  $c_s$  concentration like this. How we get? We do this one. So equation 9 we have just now seen,  $R = 1 - \frac{c_2}{c_1}$ . So from here  $1 - R = \frac{c_2}{c_1}$  or  $c_2 = (1 - R)c_1$ . And then equation number 6 we have already derived, so this  $\ln\left(\frac{c_s - c_2}{c_1 - c_2}\right) = \frac{v}{k_c}$ , this we have already derived. This is equation number 6.

So now what we do? We take exponential either side, so then we get this one. And now from here, from this part  $c_1 - c_2$  what we do? We take  $c_1$  common so that we have  $1 - \frac{c_2}{c_1}$ , rest everything keep same. So now this  $1 - \frac{c_2}{c_1}$  what we can write? We can write it as R from equation number 9, so whatever the  $c_1$ , R, that you can take it to the right hand side. So  $c_s - c_2 = c_1 R \cdot \exp\left(\frac{v}{k_c}\right)$ , that is  $c_s = c_2 R \cdot \exp\left(\frac{v}{k_c}\right)$  we can write and then from equation number 9 we can also write  $c_2 = (1 - R)c_1$ . So in place of  $c_2$  you substitute  $(1 - R)c_1$  and then plus

$c_1 R \cdot \exp\left(\frac{v}{k_c}\right)$  as it is. So now from these 2 terms if you take  $c_1$  common then  $c_s = c_1 \left(1 - R + R \cdot \exp\left(\frac{v}{k_c}\right)\right)$ . So this is what you get.

So that means if you know the retentate concentration or if you know the feed concentration you can know the surface concentration or solute concentration at the membrane surface through this expression once you have the  $\left(\frac{v}{k_c}\right)$  and  $c_1$  information along with the rejection.

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▶ If diffusion in the membrane is negligible and solute is carried through the pores by permeate flow, permeate concentration is the same as that in equilibrium with  $c_s$ , that is  $c_2$ , which is given as:  $c_2 = K c_1$  (11)

▶ Combining eqns. 9-11, leads to:  $\frac{1-R}{R} = \frac{K}{1-K} \exp\left(\frac{v}{k_c}\right) \Rightarrow$  (12)

A small diagram shows a vertical membrane with a dashed line representing the surface concentration  $c_s$  and a solid line representing the feed concentration  $c_1$ .

▶ If diffusion in the membrane is negligible and solute is carried through the pores by permeate flow, permeate concentration is the same as that in equilibrium with  $c_s$ , that is  $c_2$ , which is given as:  $c_2 = K c_1$  (11)

▶ Combining eqns. 9-11, leads to:  $\frac{1-R}{R} = \frac{K}{1-K} \exp\left(\frac{v}{k_c}\right) \Rightarrow$  (12)

$\Rightarrow c_2 = c_1 \left(1 - R + R \cdot \exp\left(\frac{v}{k_c}\right)\right) \Rightarrow$  (10)  $\Rightarrow \frac{c_2}{K} = c_1 \left(1 - R + R \cdot \exp\left(\frac{v}{k_c}\right)\right)$

$\Rightarrow \frac{c_2}{c_1} = K \left(1 - R + R \cdot \exp\left(\frac{v}{k_c}\right)\right) \Rightarrow (1-R) = K(1-R) + KR \cdot \exp\left(\frac{v}{k_c}\right)$

$\Rightarrow \frac{(1-R)}{R} = K \frac{(1-R)}{R} + K \cdot \exp\left(\frac{v}{k_c}\right) \Rightarrow \frac{(1-R)}{R} (1-K) = K \cdot \exp\left(\frac{v}{k_c}\right) \Rightarrow \frac{1-R}{R} = \frac{K}{1-K} \exp\left(\frac{v}{k_c}\right) \Rightarrow$

▶ From above eq. (12), rejection approaches 1-K as  $v/k_c$  approaches zero, and the rejection decreases with increasing flux because of concentration polarization

So if the diffusion in the membrane is negligible and solute is carried through the pores by permeate flow, permeate concentration is the same as that in equilibrium with the  $c_s$ , that is  $c_2$ .



That picture we have, right. So what we have, like you know this membrane surface we are having, right. Now here the particles are being deposited as a kind of gel layer on the membrane surface, right.

So this is  $c_1$  concentration. But other side you know  $c_2$  concentration is there, okay. So within the  $c_s$  just inside you know  $c_m$  is there, okay just outside of the pore let us say in this pore here it is  $c_m$ , here is the and then  $c_2$  is there. So this  $c_2$  and then  $c_m$ ,  $c_s$  are in a kind of equilibrium, right? Because they are just either side of the membrane.

One is just one side of the, upstream side of the membrane. Other one is the, just you know downstream of the membrane. And then within that membrane thickness layer the concentration variations are, you know, some variations are there. So that variations can be represented by the equilibrium partition coefficient and then how we can represent that?  $c_2 = Kc_s$ . Now if you use this one in equation number 11 then we get this expression for the rejection, okay.

How we get? So that also we do it here. Just now equation number 10 we derived, okay. This equation what you can do,  $c_2$ , left hand side we have  $c_s$  actually. In place of  $c_s$  let us write you know  $c_2$  by  $K$  from equation number 11. That is the first step you do, right; in place of  $c_s$  you write  $c_2$  by  $K$ . Then next step what you do? This  $K$  you take to the right hand side and this  $c_1$  you bring it to the left hand side. So left hand side you have  $\frac{c_2}{c_1}$  is equals to  $K$  multiplied by whatever the remaining step, terms, remaining terms are as it is.

Now  $\frac{c_2}{c_1}$  is what? From the equation number 9 that is rejection definition is nothing but  $(1 - R)$ , okay. In the right hand side you can just, you know write it as 2 terms,  $K(1 - R)$  as one term, and another term  $KR \cdot \exp\left(\frac{v}{k_c}\right)$ , both the terms are added here, just expanded it. Now this equation what you do, both the sides you divide by  $R$ . Both the sides you divide by  $R$ . So left hand side you have  $\frac{(1-R)}{R} = K \frac{(1-R)}{R} + K \exp\left(\frac{v}{k_c}\right)$  because  $R$  and  $R$  are from the second term would be canceled out when you are dividing it.

So now what you do, this  $\frac{(1-R)}{R}$  terms you take one side, so then you have  $\frac{(1-R)}{R}(1 - K)$  in the left hand side and then right hand side  $K \exp\left(\frac{v}{k_c}\right)$  on the right hand side. So we can write  $\frac{(1-R)}{R} = \frac{K}{1-K} \exp\left(\frac{v}{k_c}\right)$ . This is what we have, okay. So now from this equation when this  $\left(\frac{v}{k_c}\right)$  approaches 0,  $\left(\frac{v}{k_c}\right)$  approaches 0 then what we have? The exponential of 0 is 1, so that means rejection approaches  $1 - K$ . Rejection approaches  $1 - K$  and then rejection decreases with increase in flux because of the concentration polarization.

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▶ In UF of a dilute dextran solution using a tubular membrane, rejection varied from 77-93% with decreasing flux experimentally; and is in good agreement with eq. 12 and  $K = 0.044$

▶ Furthermore, for filtering solutions of moderate to high concentrations, maximum flux is low, and diffusion in pores may become important

▶ Under such conditions, the basic balance equation can be modified as:  $v c - D_e \frac{dc}{dy} = v c_2 \Rightarrow (13)$

where  $D_e$  is effective diffusivity, i.e.,  $D_e = (D_{pore} \epsilon / \tau)$  and  $y$  is the distance from membrane surface

Concentration gradient for UF system with partial rejection of solute

Further in this kind of expression whatever we have found, they are found to be kind of reliable in ultra-filtration of a dilute dextran solution using a tubular membrane, rejection varied from 77 to 93% with decreasing flux experimentally. And it is found in good agreement with the equation number 12 just we derived by substituting  $K$  is equals to 0.044. But in general what happens in the layer, filtering solutions of moderate to the high concentration, maximum flux is in general low and then diffusion in pores may become important. In some cases it is possible that the diffusion in pores is much more dominant than the other cases, right. Under such conditions how these equations would change?

So now in the previously whatever the changes were there, the concentration changes those things we have seen in this side, right. So but now this membrane layer, within this membrane layer, selective layer it is having certain thickness maybe in some microns but it is having certain thickness. In this thickness there are several pores are there. In the pores the diffusion

is dominating, right. That part we have not taken care while deriving the concentration polarization.

So under such conditions, you know what could be the equation for this  $c_s$  and  $v$  et cetera? So again we have to see the basic equation here, basic balance equation. Now what happens here, the diffusion is inside the pore. So then, at the membrane surface whatever the flux is there, that is the flux is only because of the convection if you take, so that convection is  $vc$  and other side the flux is the  $vc_2$  and that should be added with the flux due to the diffusion inside the pore, so that is  $D_e \frac{dc}{dy}$ . So  $D_e \frac{dc}{dy}$  should be added here so that if you take into the left hand side you will get this one, right.

And then  $D_e$  is nothing but effective diffusivity that  $\bar{D}_{pore} \epsilon / \tau$ , and then  $y$  is the distance from the membrane surface towards the permeate, from the membrane surface towards the permeate that is in the  $y$ , reverse  $x$  direction, so that is  $y$  here. So the membrane thickness is  $L$ . So  $y$  limits are, limits of  $y$  is nothing but  $y$  is equals to 0 here and then here  $y$  is equals to  $L$ . At  $y$  is equals to 0  $C$  is nothing but, you know  $c_s$ . At  $y$  is equals to  $L$ , you know  $c$  should be  $c_2$  but they are having some partition coefficient equilibrium, they are in equilibrium with each other. So then the corresponding concentration should be multiplied by the partition coefficient scale.

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- Integrating above eq, assuming the same partition factor at both boundaries of selective layer:  $vc - D_e \frac{dc}{dy} = vc_2 \Rightarrow (13)$

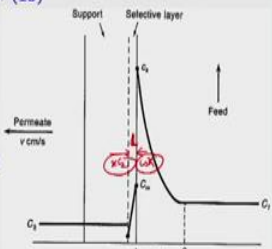
$$\Rightarrow v(c - c_2) = D_e \frac{dc}{dy} \Rightarrow \frac{v}{D_e} dy = \frac{dc}{(c - c_2)}$$

$$\Rightarrow \frac{v}{D_e} y \Big|_0^L = \ln(c - c_2) \Big|_{Kc_s}^{Kc_2}$$

$$\Rightarrow \frac{vL}{D_e} = \ln \left( \frac{Kc_2 - c_2}{Kc_s - c_2} \right) \Rightarrow \exp \left( \frac{vL}{D_e} \right) = \frac{(K - 1)c_2}{Kc_s - c_2}$$

$$\Rightarrow Kc_s \exp \left( \frac{vL}{D_e} \right) - c_2 \exp \left( \frac{vL}{D_e} \right) = (K - 1)c_2$$

$$\Rightarrow Kc_s \exp \left( \frac{vL}{D_e} \right) = c_2 \exp \left( \frac{vL}{D_e} \right) + (K - 1)c_2$$



Concentration gradient for UF system with partial rejection of solute

So now this equation we will be integrating and then applying the boundary condition exactly the same way that we have done for the concentration polarization then we have,  $v$  terms if you

take one side and D terms if you take the other side so then  $v c_2 = D_e \frac{dc}{dy}$ . Then  $\frac{v}{D_e} dy = \frac{dc}{(c-c_2)}$ , when integrate it  $\frac{v}{D_e}$ , integration of dy is y and then limits are 0 to L, 0 is the membrane surface, L is the membrane thickness towards the permeate side, okay.

So right hand side  $\ln(c - c_2)$  should be the, this thing you know, after integration of  $\frac{dc}{(c-c_2)}$  you will get  $\ln(c - c_2)$ . That limits at y is equal to 0 is the membrane surface towards the feed side, so that is at the membrane surface or the top surface, the concentration is  $c_s$  but now we are assuming the partition factor for both the boundary layers or selective layer are there.

So then k has to be multiplied, so  $K c_s$  and then towards the, inside the other side of the pore so that is here in this pore, this side; now this is layer actually. This is your thickness of the membrane, actually, L, okay. This side the surface concentration is  $c_s$ . This side moment it comes, this side other side it is  $c_2$ . But you know it has same partition coefficient, that is the assumption because we do not know exactly what is  $c_s$ , we do not know exactly  $c_2$  inside the pore, okay. So they are in equilibrium with a kind of partition coefficient K. So that has to be multiplied here.

So when we take these limits then  $\frac{vL}{D_e} = \ln\left(\frac{Kc_2 - c_2}{Kc_s - c_2}\right)$ . Then you take exponential so here  $\frac{(K-1)c_2}{Kc_s - c_2}$ , when you rearrange this equation then do the simplification you will get  $Kc_s \cdot \exp\left(\frac{vL}{D_e}\right) - c_2 \cdot \exp\left(\frac{vL}{D_e}\right) = (K-1)c_2$ . Further you take all  $c_2$  terms one side,  $Kc_s \cdot \exp\left(\frac{vL}{D_e}\right) = c_2 \cdot \exp\left(\frac{vL}{D_e}\right) + (K-1)c_2$ .

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$$\Rightarrow \frac{c_2}{c_s} = \frac{K \cdot \exp\left(\frac{vL}{D_e}\right)}{K - 1 + \exp\left(\frac{vL}{D_e}\right)} \Rightarrow (14)$$

where  $L$  is the thickness of the selective layer

- ▶ If  $vL/D_e$  is less than 2, then solute diffusion will have a significant effect on the rejection
- ▶ Since the diffusion lowers the rejection at low permeate flux and concentration polarization is important at high flux, fraction rejected is predicted to go through a maximum with permeate flux

This equation, if you write  $\frac{c_2}{c_1} = \frac{K \cdot \exp\left(\frac{vL}{D_e}\right)}{K - 1 + \exp\left(\frac{vL}{D_e}\right)}$ . This is what we have this equation for a surface concentration if the pore diffusion is predominating. If the pore diffusion is predominating, under such condition the surface concentration on the membrane surface can be obtained by this expression. Or the relation between the surface concentration and permeate flux can be written as this equation number 14. So  $L$  is the thickness of the selective layer, that membrane thickness.

If  $\frac{vL}{D_e}$  is less than 2 then the solute diffusion will have a significant effect on the rejection and then  $\frac{vL}{D_e}$  value goes further beyond 2, it is going to have a pore diffusion is going to take the lead. Since diffusion lowers the rejection at low permeate flux and concentration polarization is important at high flux, fraction rejected is predicted to go through a kind of maximum with the permeate flux.

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References for this lecture are given here but most of the notes is prepared from this first reference book McCabe, Smith and Herriot, Unit Operations of Chemical Engineering. Thank you.