Introduction to Process Modeling in Membrane Separation Process

Prof. Sirshendu De
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Lecture – 05
Modeling of Reverse Osmosis

I welcome you all in this session, as you have seen in the earlier classes that we have defined the basic principles of Separation Processes. Definition of the separation processes and what are the membrane based processes, difference between the rates governed process in the equilibrium governed process and we also have seen the categorization of various membrane based processes and what are the typical differences and solute features of each of this process that we have already seen. Then we have gone through is rise of definitions of various terms those are quite important during the course of this structure.

So, we have already known about the basic terms those will be appearing in the modeling. Therefore, now we are quail equipment to start with the modeling of the various processes. And modeling simply means we would like to predict the system performance. And what is the system performance? The system performance is in terms of througput of the process that is the permeate flux and the permeate quality, that is what is the solute concentration in permeate.

So, these two are the basic indicators of the system performance, because if we can may measure or predict the permeate flux quite accurately that will be helping us tremendously in design of scaled up version. We will be conducting experiments in a small scale and then will be modeling the whole system and compare our computed data with the experimental data. If that matches quite will then we will say that our modeling is validated. Once will be using a validated model for skilling up, then we can get the permeate flux and is scaled up version. Once you get a scaled up version of permeate flux that what is the meter cube permeated square per second or it is call (Refer Time: 02:21) liter permeated square hour of flux.

Then if we have some design in your mind that what is it the througput of the process should be let us say500 liter per day or 1000 liter per day or 10000 liter per day then we can divide the product where productivity of this way 5000 liter per day divided by permeate flux; that will be giving of the effective filtration area or membrane area. Once we know these much membrane area is required we can really go for that much of membrane area or we can procure a model which will be conforming that membrane area. So, that will be very very important in skilling up with the process.

Similarly, apart from the througput for commercial viability the permeate quality is very very important, because in most of the applications we have to conform the quality of the filtrate or permeate to particular nobe. For example, if we would like to have to build up a plant of cadmium removal which will be basically treatment of a flint form coming out from ternary of a leather industry it continuous toxic equilibrium and the permissible level of toxic equilibrium in any surface water is around 2 milligram per liter.

So, your concentration of equilibrium in the filter should be less than 2 milligram per liter. So that whether in your actual system that is really coming out or not that will have to see. If its concentration is around 5 or 10 milligram per liter in the filtrate then that is not viable that is not that is not. So, permeate, the process performance is basically indicate by 2 parameters througput is the permeate flux and permeate quality or the solute concentration in permeate.

If this two are properly done, if you can model this system quite accurately then we can do away with a number of experiments, so if we can get in for this data if we conduct experiments over a wide range of operating conditions, but to conducts so many experiments with that will be investing the man power will be investing money man power resources and energy. In order to minimize that will be conducting less number of experiments and conform our model and then we can conduct the virtual experiments in terms of the simulation and process modeling.

So, there lies the importance of modeling and simulation. Therefore the in order to predict the system performance quite accurately for scaling up of the system of the process; so first will be looking into the modeling of an RO system.

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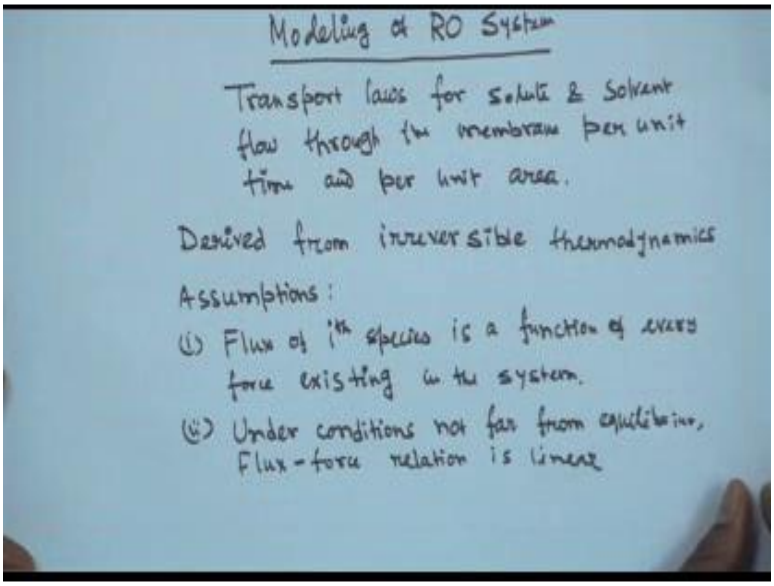

Modeling of RO System

Transport laws for solute & solvent flow through the membrane per unit time and per unit area.

Derived from irreversible thermodynamics

Assumptions:

(i) Flux of i^{th} species is a function of every force existing in the system.

(ii) Under conditions not far from equilibrium, Flux-force relation is linear

RO system; and we will be basically writing down the transport laws for solute and solvent flow through the membrane per unit time and per unit area. These laws are derived from irreversible thermodynamics.

There are couples of assumptions involved. So, let as write down the assumptions involved in the process or in the in the derivations. First one is, flux of ith species is a function of every force existing in the system. Second one is, under conditions not far from equilibrium flux force relationship is linear. That means, if we consider that flux is proportional to the driving force and that relationship is linear if we consider not far from equilibrium.

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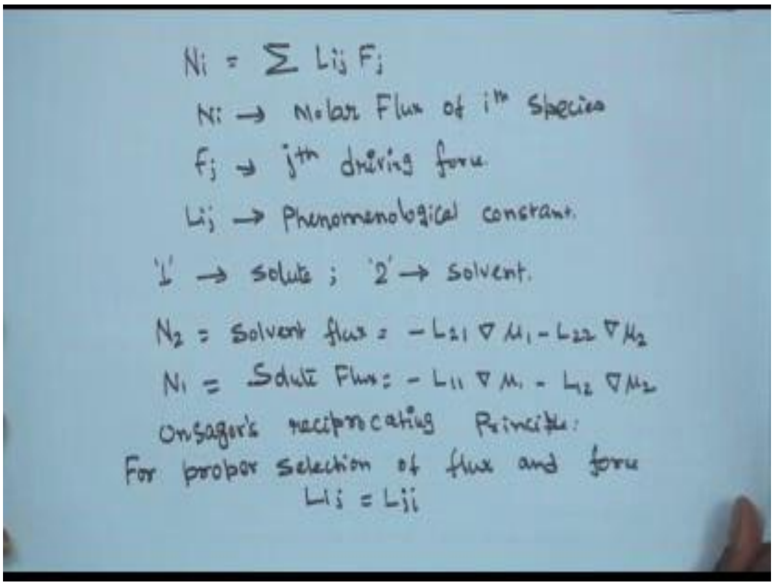

$N_i = \sum L_{ij} F_j$

$N_i \rightarrow$ Molar Flux of i^{th} Species

$F_j \rightarrow$ j^{th} driving force

$L_{ij} \rightarrow$ Phenomenological constant.

'1' → solute ; '2' → solvent.

N_2 = Solvent flux = $-L_{21} \nabla \mu_1 - L_{22} \nabla \mu_2$

N_1 = Solute Flux = $-L_{11} \nabla \mu_1 - L_{12} \nabla \mu_2$

Onsager's reciprocating Principle:

For proper selection of flux and force

$L_{ij} = L_{ji}$

So, we can write that Ni there is a solute flux is summation of Lij times Fj. Where, Ni is the Molar Flux of ith species and Fj is jth driving force. And the constant Lij as we have discussed earlier it will be a proportionally constant and that will be nothing but the Phenomenological constant. Now, we use a notation 1 stands for solute and 2 stand for solvent. So, solvent flux can be written has minus L 21 gradient of mu 1 minus L 22 gradient of mu 2, because in our system what is the force is the gradient of chemical potential. And similarly we can write solute flux is minus L 11 gradient of mu 1 minus L 12 gradient of mu 2.

Then we have something call Onsager's reciprocating principle. Here we say if flux and forces are properly selected; for proper selection of flux and force Lij will be nothing but Lji. Then comes the concept of coupling.

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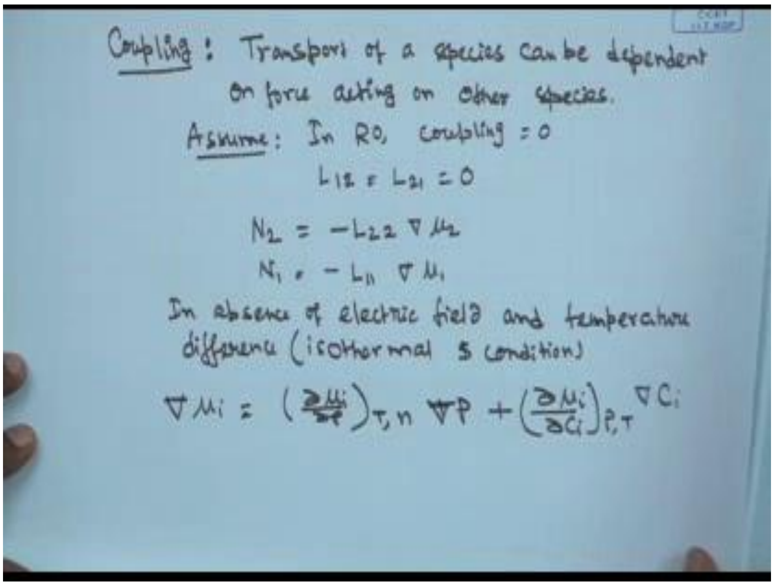

Coupling: Transport of a species can be dependent on force acting on other species.

Assume: In RO, coupling = 0

$$L_{12} = L_{21} = 0$$

$$N_2 = -L_{22} \nabla \mu_2$$

$$N_1 = -L_{11} \nabla \mu_1$$

In absence of electric field and temperature difference (isothermal 5 condition)

$$\nabla \mu_i = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} \nabla P + \left(\frac{\partial \mu_i}{\partial C_i}\right)_{P,T} \nabla C_i$$

And what is the definition of coupling. Coupling sizes that we due to existence of forces present on another species come influence the transport of a particular species. That means, transport of a species can be dependent on force acting on other species. There is a definition of coupling and we assume again we will be having an assumption here. Assume that the coupling in reverse osmosis in RO the coupling is 1. There is no existence of coupling. Therefore, L 12 and L 21 equal to 0, and will be having the expression of solvent flux as minus L 22 grad of mu 2 and N 1 is equal to minus L 11 grad of mu 1.

Now gradient of chemical potential in absence of in electric field it will be described as, in absence of electric field and temperature difference; because most of the membrane separation process or occurring under isothermal conditions, temperature difference absence of temperature difference means it is basically isothermal situation. We are dealing with isothermal situation.

So, expression of grad of mu i is written has delta mu i del P constant t and n plus grad of P plus del mu i del Ci constant pressure and temperature gradient of Ci. Therefore, we are in a position to write down the solvent flux as.

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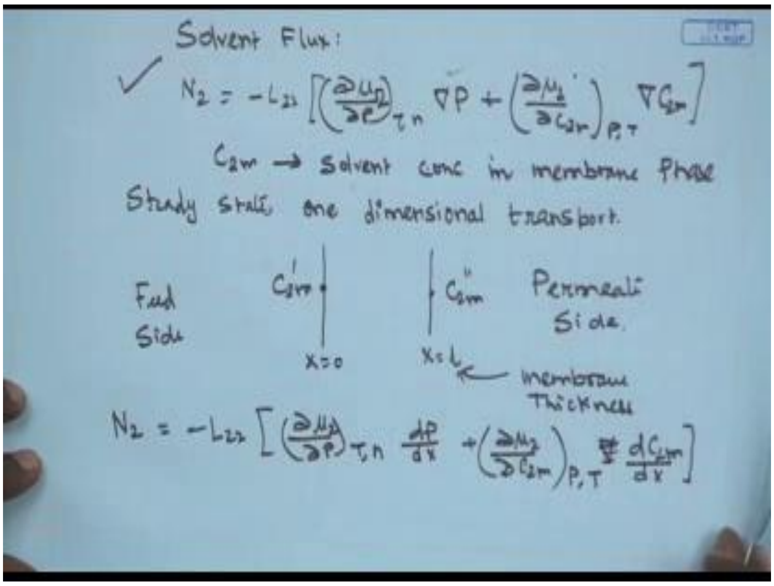

Solvent Flux:

✓ $$N_2 = -L_{22}\left[\left(\frac{\partial \mu_2}{\partial P}\right)_{T,n} \nabla P + \left(\frac{\partial \mu_2}{\partial C_{2m}}\right)_{P,T} \nabla C_{2m}\right]$$

$C_{2m} \rightarrow$ Solvent conc in membrane Phase

Steady state, one dimensional transport.

$$N_2 = -L_{22}\left[\left(\frac{\partial \mu_2}{\partial P}\right)_{T,n} \frac{dP}{dx} + \left(\frac{\partial \mu_2}{\partial C_{2m}}\right)_{P,T} \frac{dC_{2m}}{dx}\right]$$

So, solvent flux can be written has N 2 is equal to minus L 22 gradient del mu 1 del P t and n grad of del P plus, so this is del mu 2; so del mu 2 del C 2m pressure constant pressure temperature gradient of C 2m. So, what is C 2m? C 2m is constant solvent concentration in membrane phase or in the solid phase.

So, we assume again is steady state and one dimensional transport. Let us write down the system geometric and axis this x equal to l 0 and the x equal to l, l is the membrane thickness, so this is nothing but the membrane thickness. C 2m prime is solvent concentration of species two on the membrane surface in the upstream or the feed side. Feed side and C 2m double prime is concentration of solute number or solute two on the membrane surface in the filtrate or permeate side.

Now, we will be considering a one dimensional and steady state system and therefore we can expand this equation. These in this equation we can write delta P has d p d x and delta C 2m as d C 2m d x, and then integrate along the with d x. So, we can write it has N 2 is equal to minus L 22 del mu 2 del P constant t and n d p d x plus del mu 2 del C 2m constant P and T gradient of, we just write d C 2m d x. Then we integrate both sides over d x and see what you guess.

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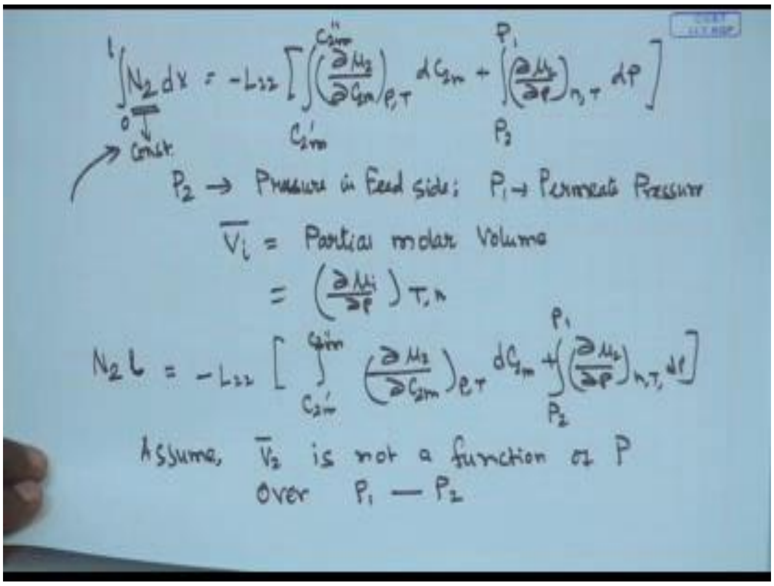

$$\int_0^l \underbrace{N_2}_{\text{Const.}} dx = -L_{22}\left[\int_{C'_{2m}}^{C''_{2m}} \left(\frac{\partial \mu_2}{\partial C_{2m}}\right)_{P,T} dC_{2m} + \int_{P_2}^{P_1} \left(\frac{\partial \mu_2}{\partial P}\right)_{n,T} dP\right]$$

$P_2 \rightarrow$ Pressure in Feed side; $P_1 \rightarrow$ Permeate Pressure

$$\bar{V}_i = \text{Partial molar Volume} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n}$$

$$N_2 l = -L_{22}\left[\int_{C'_{2m}}^{C''_{2m}} \left(\frac{\partial \mu_2}{\partial C_{2m}}\right)_{P,T} dC_{2m} + \int_{P_2}^{P_1} \left(\frac{\partial \mu_2}{\partial P}\right)_{n,T} dP\right]$$

Assume, $\bar{V}_2$ is not a function of P over $P_1 - P_2$

So, N 2 d x is equal to minus L 22 del mu 2 del C 2m constant P and t d C 2m plus del mu to del P constant n and t d P. And then we integrate across the length of the membrane thickness of the membrane 0 to l. So, this C 2m will be from C 2m prime to C 2m double prime and these will be form P upstream to it downstream, so P 2 to P 1. And P 2 is the pressure in the feed side and P 1 is permeate pressure permeate pressure.

So, let us defined the partial molar volume, will be del mu i del P at constant t and n. So, using these definitions of molar volume we can integrate this equation and get N 2 is constant at the steady state. So, we can write N 2 times l is equal to minus L 22 C 2m prime to C 2m double prime del mu 2 del C 2m constant P and t d C 2m plus; del mu 2 del P we can we can substitute as in terms of the molar volume del mu 2 del P n and t d p and they will form P 2 to P 1. Then we can substitute the definition of partial molar volume by del mu to del P and assume that V 2 bar the partial molar volume is not a function or pressure over the range P 1 to p two. If we assume that V 2 bar, partial molar volume of solvent is constant over the pressure range P 1 to P 2 that we are considering.

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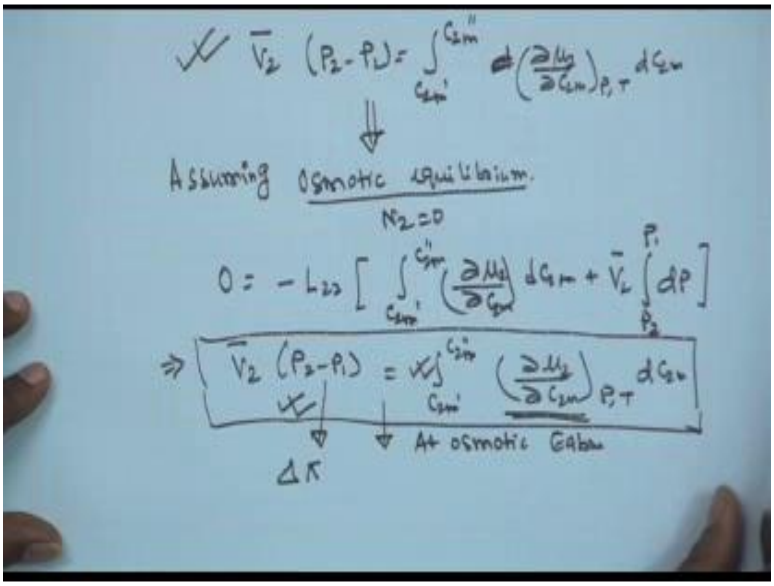

$$\bar{V}_2 (P_2 - P_1) = \int_{C_{2m}'}^{C_{2m}''} \left(\frac{\partial \mu_2}{\partial C_{2m}}\right)_{P,T} dC_{2m}$$

$$\Downarrow$$

Assuming osmotic equilibrium.

$$N_2 = 0$$

$$0 = -L_{22}\left[\int_{C_{2m}'}^{C_{2m}''} \left(\frac{\partial \mu_2}{\partial C_{2m}}\right) dC_{2m} + \bar{V}_2 \int_{P_2}^{P_1} dP\right]$$

$$\Rightarrow \boxed{\bar{V}_2 (P_2 - P_1) = \int_{C_{2m}'}^{C_{2m}''} \underline{\left(\frac{\partial \mu_2}{\partial C_{2m}}\right)}_{P,T} dC_{2m}}$$

$\Delta \pi$

At osmotic Eqbm

So, once we do that then we can integrate out from the definition of the molar volume as V 2 bar multiplied by P 2 minus P 1 is equal to C 2m prime to C 2m double prime del mu 2 del C 2m at constant pressure and temperature times d C 2m. Now this equation is arrived assuming the osmotic equilibrium. When the osmotic equilibrium is reached N 2 is equal to 0 and in the above expression we can put 0 is equal to minus L 22 C 2m prime to C 2m double prime del mu 2 del C 2m d C 2m plus, del mu 2 del P we can substitute it from the using the definition of partial molar volume; so, V 2 bar from P 2 to P 1 that will be treated as constant because it will be constant over the pressure range times d p. So, once you do that doing we get the simplification, we can get this relationship that V 2 bar is P 1 and P 2 into the other side; P 2 minus P 1 is equal to C 2m prime to C 2m double prime del mu to del C 2m constant pressure and temperature d C 2m.

So, we get these relationship what exactly we have written here assuming the osmotic equilibrium. In fact, this is one of the expressions of del mu 2 del C 2m P 1 t d C 2m and the osmotic equilibrium. This equation can be treated as a boundary condition of the limit of the governing equation of N 2. Therefore, in the governing equation of solvent flux we can substitute this term the integral C 2m prime to C 2m double prime del mu 2 del C 2m d C 2m by these expression V 2 bar into P 2 minus P 2.

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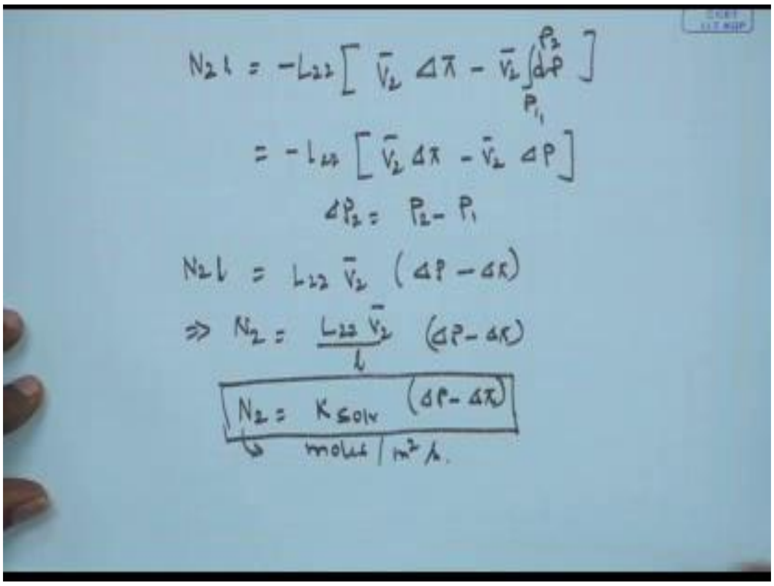

$$N_2 l = -L_{22}\left[\bar{V}_2 \Delta\pi - \bar{V}_2 \int_{P_1}^{P_2} dP\right]$$

$$= -L_{22}\left[\bar{V}_2 \Delta\pi - \bar{V}_2 \Delta P\right]$$

$$\Delta P_2 = P_2 - P_1$$

$$N_2 l = L_{22} \bar{V}_2 (\Delta P - \Delta\pi)$$

$$\Rightarrow N_2 = \frac{L_{22}\bar{V}_2}{l}(\Delta P - \Delta\pi)$$

$$\boxed{N_2 = K_{solv}(\Delta P - \Delta\pi)}$$

↳ moles / m² h.

So, if you really do that in what will be getting is that N 2 l is equal to minus L 22 V 2 bar. And what is this? This will be at osmotic equilibrium, P 2 minus P 1 will be nothing but the delta pi; it will be nothing but the osmotic pressure difference. So, since we are evaluating this term at the equilibrium condition the P 2 minus P 1 will be nothing but the osmotic pressure difference across the membrane.

So therefore, we can now write down the governing equation of solvent flux as N 2 l is equal minus L 22 V 2 bar times delta pi minus V 2 bar del P d p from P 1 to p two. Therefore, these will be minus L 22 V 2 bar delta pi minus V 2 bar delta P, where delta P is nothing but P 2 minus P 1 at P 2 is the higher pressure. P 2 is the pressure in the feed side P 1 is the pressure in the filtrate side.

So now, we can consume minus sign within the bracket so this becomes L 22 V 2 bar is equal to delta P minus delta pi and N 2 is equal to L 22 V 2 bar divided by l delta P minus delta pi. Now L 22 is a constant V 2 bar is a constant because it is the molar volume of the solid or of the solvent for a particular membrane thickness is constant so the whole thing will become a constant and these will be nothing but some constant k solvent multiplied by delta P minus delta pi.

Now these is the governing law of solvent transport through the porous membrane and the unit of N 2 is basically the moles bar meter square a membrane area per unit time. Now, this can be converted into gram per meter square per second if we multiplied into the molecular weight and then if we invoke the term of density this flux can be written in terms of the volumetric flux.

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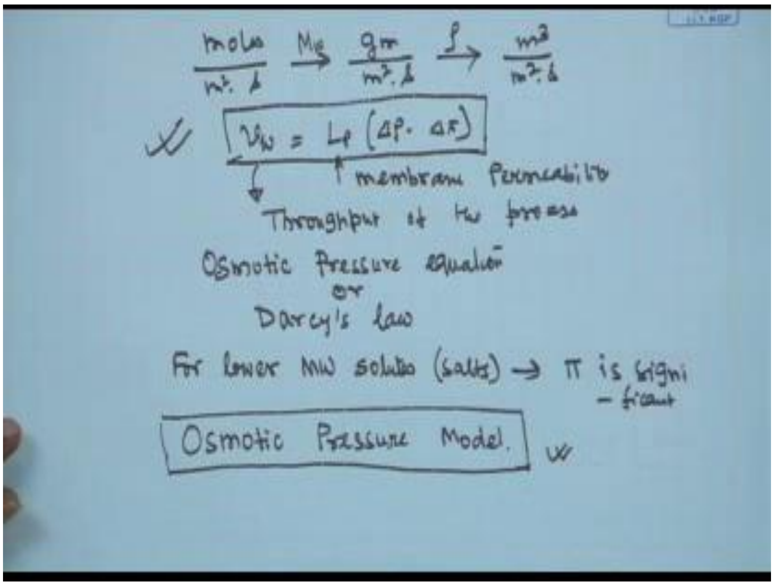

$$\frac{moles}{m^2.s} \xrightarrow{M_w} \frac{gm}{m^2.s} \xrightarrow{\rho} \frac{m^3}{m^2.s}$$

$$\boxed{v_w = L_p(\Delta P - \Delta \pi)}$$

membrane Permeability

Throughput of the process

Osmotic Pressure equation

or

Darcy's law

For lower MW solutes (salts) → π is signi-ficant

Osmotic Pressure Model.

So, moles per moles per meter square per unit time can be converted into the grams per meter square per unit time by using a factor of molecular weight, and then these can be converted into meter cube per meter square second by using a factor of density. Therefore, we can really express our volumetric flux as v w is nothing but Lp del P minus del pi. Where, Lp is the membrane permeability. This gives the transport law of the volumetric flow rate of the solvent through the membrane and this has a direct bearing of the througput of the process.

Since these expression of permeate flux involves the osmotic pressure and the operating pressure and the permeability of the membrane this law is known as the osmotic pressure equation or this is also known as the so called Darcy’s law through the porous medium. And since for the solutes having the lower molecular weight; for lower molecular solutes like salts osmotic pressure is significant. And this is the governing equation of volumetric flow rate through the membrane and this model is also known as the osmotic pressure model.

So, next from the irreversible thermodynamics under certain assumptions we have modeled the volumetric flow through volumetric flow rate of the solvent through the porous media basically it is not the flow rate it is basically the flow permeate flux and the that is that will be through the osmotic pressure model. Next what will be doing, will be calculating the similar type of exercise in order took quantify the solute flux through the porous membrane.

Thank you very much.