Membrane Technology
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Lecture-13
Transport Through Porous Membranes

Good morning students today is lecture 13 of module 5. So in this will discuss the transport through porous membranes, like transport of gases Knudsen flow. Then we will discuss a model which is also known as friction model, then non porous membrane transport and we will also discuss the solution diffusion model.

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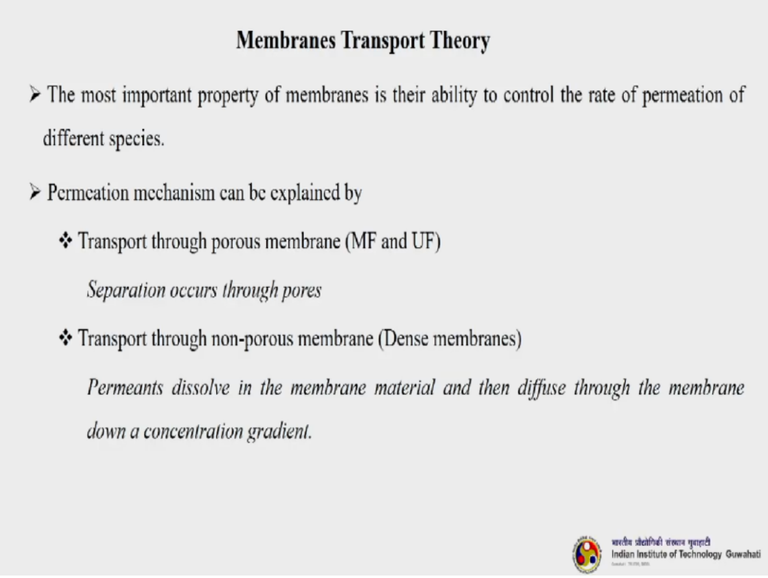

Membranes Transport Theory

- ➢ The most important property of membranes is their ability to control the rate of permeation of different species.
- ➢ Permeation mechanism can be explained by
  - ❖ Transport through porous membrane (MF and UF)

    Separation occurs through pores
  - ❖ Transport through non-porous membrane (Dense membranes)

    Permeants dissolve in the membrane material and then diffuse through the membrane down a concentration gradient.

As you know, the most important property of membrane is their ability to control the rate of permeation of the different species. Now permeation can be explained by 2 mechanisms. So, one is that if we talk about the porous membrane, which is essentially the microfiltration and ultrafiltration membranes, so, in which the separation is occurring through the pores and in another categories the non porous membrane, so, or also you can call them dense membranes. So, here what is happening now, the permeant?

Which is supposed to be transported through the membrane is first dissolves itself in the membrane material, then diffuses through the membrane onto the permeate site. And due to the concentration gradient, so, essentially we have clubbed this transport into 1different categories.

We will discuss the transport of porous membrane and then we will discuss the transport of the non porous membrane.

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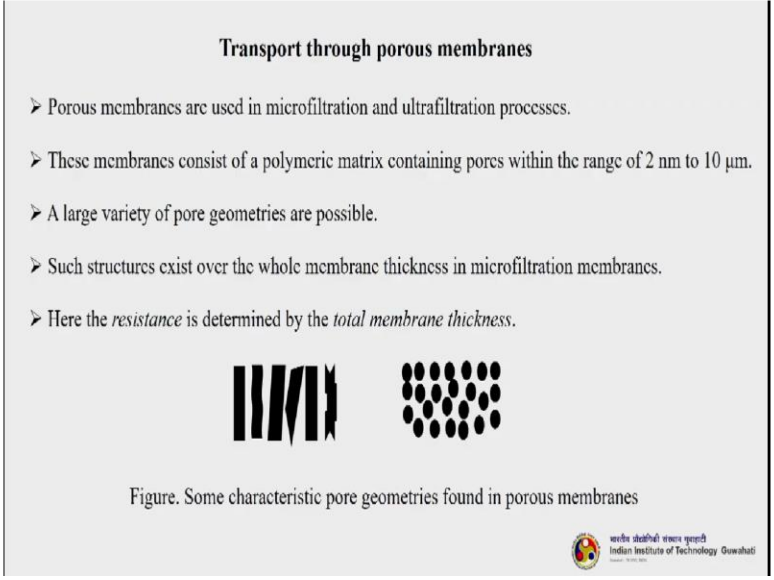

Transport through porous membranes

- Porous membranes are used in microfiltration and ultrafiltration processes.
- These membranes consist of a polymeric matrix containing pores within the range of 2 nm to 10 μm.
- A large variety of pore geometries are possible.
- Such structures exist over the whole membrane thickness in microfiltration membranes.
- Here the *resistance* is determined by the *total membrane thickness*.

Figure. Some characteristic pore geometries found in porous membranes

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So, porous membranes are used in microfiltration and ultrafiltration processes. These membranes consist of a polymeric matrix containing pores within the range of 2 nanometer to10 micrometers. So, these things we have discussed ever since, in this particular lectures. Also, I am just saying to give you a little idea about what are the porous and non porous membranes we will discuss little briefly very briefly, So that you do not have to go back and see the earlier videos of the lectures.

So, here since we talk about pores as you know that we have discussed many times the different types of pores geometries are possible. So, such structures exist over the whole membrane thickness in micro filtration membrane. Now, in micro filtration membrane that resistance is determined by the total membrane thickness. So, as I told you in the last class also the thickness of the membrane material places the very important role and more the thickness the more with the resistance to the transport or the flow.

So, you can see there are 2 different types of pore geometries that I have seen, you can see these are mostly cylindrical types of pores. And which are actually in real life practices are nonexistence or they are not present in that type in exactly something like this. So this is just a trying to make you understand that how force maybe and then of course, we can have something some pores like this also distributed uniformly or heterogeneous also.

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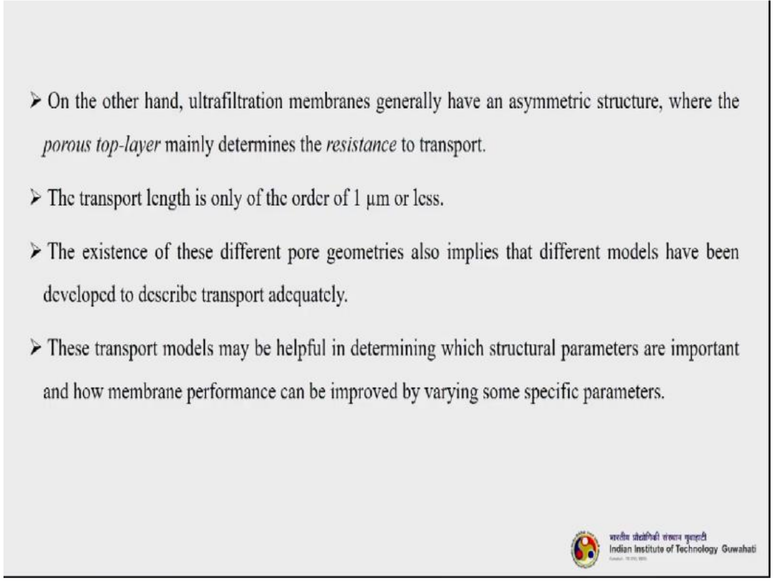

- On the other hand, ultrafiltration membranes generally have an asymmetric structure, where the *porous top-layer* mainly determines the *resistance* to transport.
- The transport length is only of the order of 1 μm or less.
- The existence of these different pore geometries also implies that different models have been developed to describe transport adequately.
- These transport models may be helpful in determining which structural parameters are important and how membrane performance can be improved by varying some specific parameters.

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So, this is about microfiltration an ultrafiltration membrane, it is usually a being in asymmetric structure though it is porous, but it is asymmetry. So, when the porous top layer mainly determines the resistance to flow. So, both the layers are porous in ultrafiltration membranes the transport length is only the order of 1 micron or less so, is minimum the thickness of the top layer the resistance to transport will be much lower.

Now, the existence of these different pore geometries also implies that different models have been developed to describe transport adequately. So, due to the different types of pore geometries, pore sizes and all those are actually available in real life practices. That is why different models are also been done. Now, these transport models may be helpful in determining which structural parameters are important and how membrane performance can be improved by varying some specific parameters.

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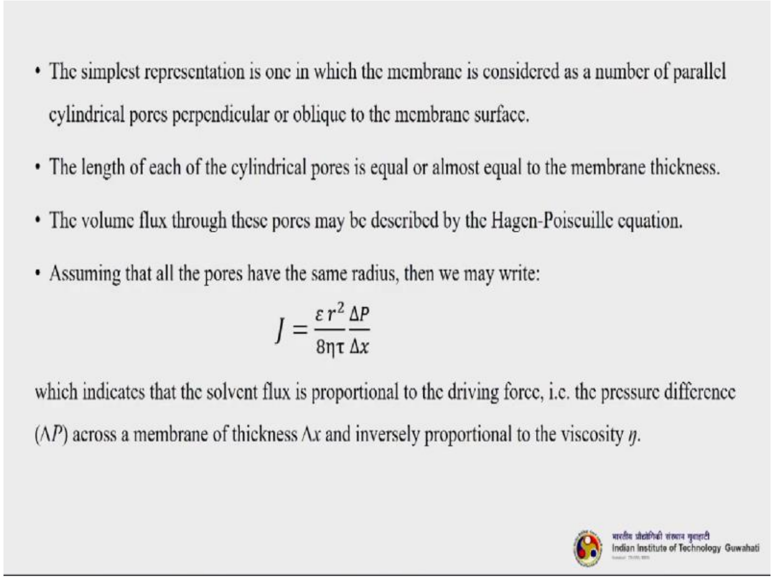

- The simplest representation is one in which the membrane is considered as a number of parallel cylindrical pores perpendicular or oblique to the membrane surface.
- The length of each of the cylindrical pores is equal or almost equal to the membrane thickness.
- The volume flux through these pores may be described by the Hagen-Poiseuille equation.
- Assuming that all the pores have the same radius, then we may write:

$$J = \frac{\varepsilon r^2}{8\eta\tau}\frac{\Delta P}{\Delta x}$$

which indicates that the solvent flux is proportional to the driving force, i.e. the pressure difference (ΔP) across a membrane of thickness Δx and inversely proportional to the viscosity η.

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The simplest representation is one in which the membrane is considered as a number of parallel cylindrical pores this we have already known. So, if you remember the recall the Hagen Poiscuille equation this is the equation in which it is assume that the pore sizes they are parallel cylindrical pores perpendicular or oblique to the membrane surface. Now, the length of each cylindrical pore is equal or almost equal to the membrane thickness and the volume flux through these pores may be described by this Hagen Poiscuille equation.

If you assume that all pores of the same radius then we can write this equation it is J equals to J is the volumetric blocks epsilon r square, then 8, this is viscosity, tau and delta p / delta x. So delta p / delta x the actual the gradient and this indicates that solvent flux is proportional to the driving force that is the pressure difference across the membrane thickness delta x and inversely proportional to the viscosity.

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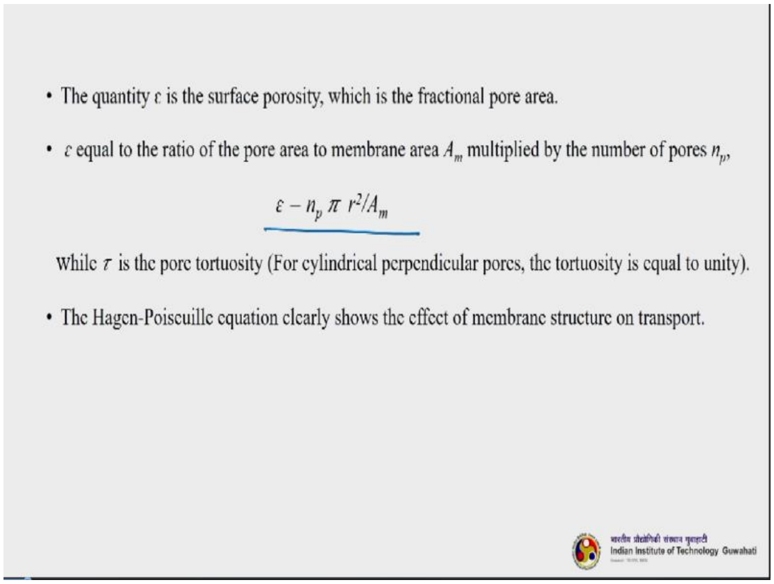

- The quantity ε is the surface porosity, which is the fractional pore area.
- ε equal to the ratio of the pore area to membrane area A_m multiplied by the number of pores n_p,

$$\underline{\varepsilon - n_p \pi r^2/A_m}$$

While τ is the pore tortuosity (For cylindrical perpendicular pores, the tortuosity is equal to unity).

- The Hagen-Poiseuille equation clearly shows the effect of membrane structure on transport.

The quantity epsilon is the surface porosity, which is also called the fractional pore area. Now, that epsilon is equal to the ratio of the pore area to the membrane area multiplied by the number of pores. So, you can calculate epsilon from using this equation n p pi r square / A m. So, n p is the number of pores that is present on the membrane surface, pi r square is the area of the pore and A m is the area of the membrane. And tau is actually the pore tortuosity for cylindrical perpendicular pores, the tortuosity is equal to 1.The Hagen Poiscuille equation clearly shows the effect of membrane structure on transport.

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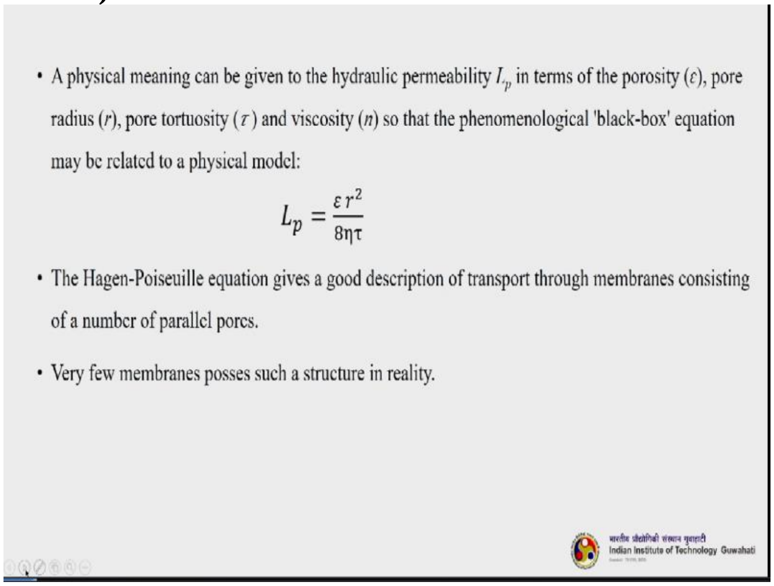

- A physical meaning can be given to the hydraulic permeability L_p in terms of the porosity (ε), pore radius (r), pore tortuosity (τ) and viscosity (n) so that the phenomenological 'black-box' equation may be related to a physical model:

$$L_p = \frac{\varepsilon r^2}{8\eta\tau}$$

- The Hagen-Poiseuille equation gives a good description of transport through membranes consisting of a number of parallel pores.
- Very few membranes posses such a structure in reality.

So, a physical meaning can be given to hydraulic permeability in terms of porosity pore radius pore tortuosity and viscosity. So that the phenomenological black box equation may be related to a physical model, because you remember last class we discussed that about the phenomenological equations, the proportionality constant and all so, you know the phenomenological equations are there actually black box equations and they are not telling anything about how the transport is occurring.

So, what they are telling is that how further transport that proposnality constant a, tells us that how fast a permeant will permeate through the membrane, it is not telling how it is happening. So, the mechanism is not being taught. So, unless until we take into account the pore size pore geometries, then, the tortuosity or the which will give us the pore on this one, the shape and sizes, sips of the pores, then, membrane material and viscosity.

So, many parameters are there. So, then we cannot understand what is the actual mechanism when a particular permeant is passing through the transporting through the membrane. So, though the Hagen Poiseuille is a question that gives a good description of the transport through the membrane consisting of a number of parallel pores, but please again remember that this is an assumption real assumption, which is not true in real practice, but see when you define derived or developed certain models or equations, then you need to have some assumptions

So, based on that assumption only we have proceeding either we can have a Hagen Poiseuille education or we can go for a Kozeny Carman equation, So, still they are for better than the year phenomenological equations because they do not have absolute to tell us anything about how the transport actually is happening.

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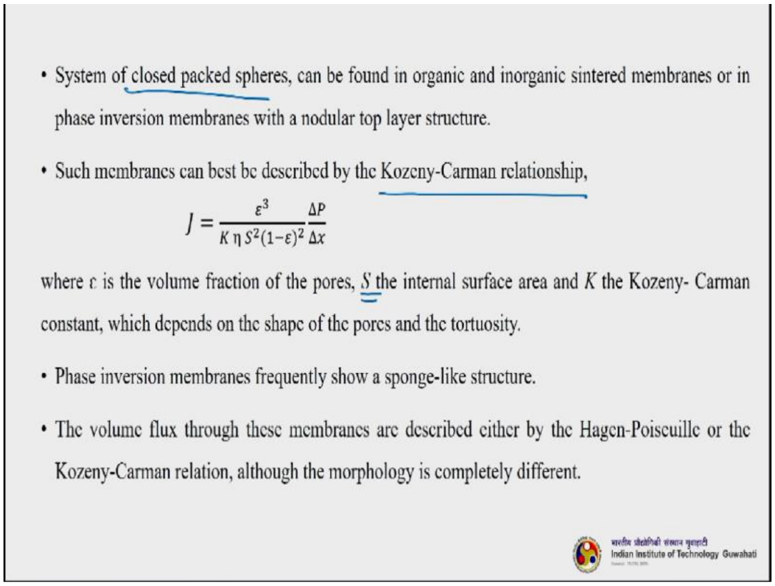

- System of closed packed spheres, can be found in organic and inorganic sintered membranes or in phase inversion membranes with a nodular top layer structure.
- Such membranes can best be described by the Kozeny-Carman relationship,

$$J = \frac{\varepsilon^3}{K\,\eta\,S^2(1-\varepsilon)^2}\frac{\Delta P}{\Delta x}$$

where ε is the volume fraction of the pores, S the internal surface area and K the Kozeny- Carman constant, which depends on the shape of the pores and the tortuosity.

- Phase inversion membranes frequently show a sponge-like structure.
- The volume flux through these membranes are described either by the Hagen-Poiseuille or the Kozeny-Carman relation, although the morphology is completely different.

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So, system of closed packed spheres which can be found in organic and inorganic sintered membranes, usually in ceramic membranes, or in phase inversion membranes with a nodular top layer structure. So, if you take assume that the pores are actually to that intersperses between the closed packed spheres that is the assumption of the Kozeny Carman equation. So, here epsilon is the volume fraction of the pore S is the internal surface area and k is the Kozeny Carman constant which it again depends on the shape of the pores and the tortuosity.

Now phase inverse membranes frequently show a sponge like structure, the volume flux through these membranes are described either by the Hagen Poiseuille or the Kozeny Carman relation, although morphology is completely different.

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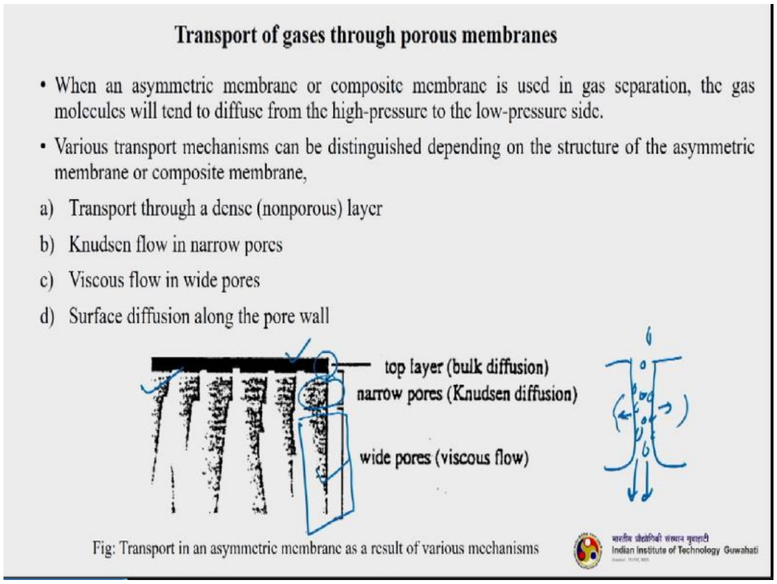

Transport of gases through porous membranes

- When an asymmetric membrane or composite membrane is used in gas separation, the gas molecules will tend to diffuse from the high-pressure to the low-pressure side.
- Various transport mechanisms can be distinguished depending on the structure of the asymmetric membrane or composite membrane,

a) Transport through a dense (nonporous) layer
b) Knudsen flow in narrow pores
c) Viscous flow in wide pores
d) Surface diffusion along the pore wall

Fig: Transport in an asymmetric membrane as a result of various mechanisms

When an asymmetric membrane or composite membrane is used in gas separation, the gas molecules will tend to diffuse from the high pressure to the low pressure side. So, the various mechanisms can be distinguished depending on the structure of the asymmetric membrane now, please look at this particular membrane structure you can see there is a top layer here, that is followed by another sub layer of a relatively big size or large you can say, which is consisting of narrow pores.

Then there is another one which is this one which is containing wide pores. So, that is the thickness will be more. So, this is how the asymmetric membrane prepares. So, it cannot many times it happened that we have only the top layer and this layer we do not have an intermediate narrow pore layer. Now, if you look closely look at how the transport is happening if you see the first top layer.

So, the bulk diffusion occurring, in that it is very thin as thin as possible so, that the thickness so, that the thickness of the membrane plays a very or provides a very less resistance to the flow.
Now, when you come down next about this particular layer, where the pores are narrows here seems the pores are small. So, the Knudsen diffusion will be prevalent. Again when we are going down to the next particular layer, in which the pores are wide pores. So here, more or less you can say these are microfiltration membranes.

So, here the transport will occurred through the viscous flow. So, the pore is not at all impacting any resistance to the flow and then there are another thing that also happens which is called surface diffusion. Surface diffusion along the pore wall so, let us say this is a particular pore wall when the permeates are passing like this. So, it will happen that they are getting attached to the surface, then they will slowly diffuse certain electron also, they may diffuse here this side also, depending upon what is the structure here.

So, the surface diffusion cannot be ruled out. So, that is also takes place and that is also important when you describe a transport or describe the transport through asymmetric membrane. So, top layer which is if it is a non porous layer, then it is bulk diffusion, then followed by the 2nd layer Which is having narrow pores, which is Knudsen diffusion and then the widest wide pores which is actually microfiltration range that will be discussed.

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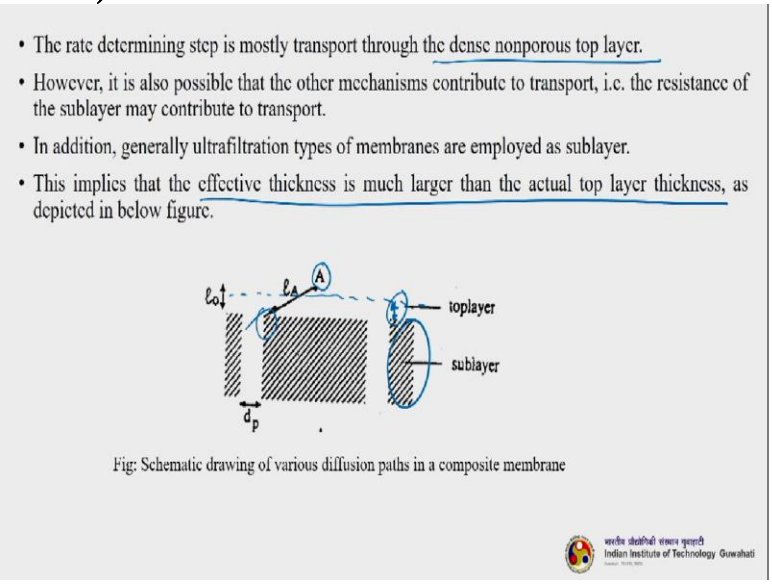

- The rate determining step is mostly transport through the dense nonporous top layer.
- However, it is also possible that the other mechanisms contribute to transport, i.e. the resistance of the sublayer may contribute to transport.
- In addition, generally ultrafiltration types of membranes are employed as sublayer.
- This implies that the effective thickness is much larger than the actual top layer thickness, as depicted in below figure.

Fig: Schematic drawing of various diffusion paths in a composite membrane

However, the rate determining step is mostly transport through the dense non porous top layer so, here actual separation is happening due to the top layer which is non porous layer. However, it is also possible that other mechanisms contribute to transport that is the resistance of the sub layer may also contribute to the transport now, we will see how it actually happens. So, in addition generally ultrafiltration types of membranes are also employed as sub layer in certain cases. So, these are specific cases.

So, this implies that effective thickness is much larger than the actual top layer thickness, so you can see this there is a top layer here which is not properly being shown here. So, this is your top this is the top layer.So then there is a sub layer here. So, you can see this what is essentially is being told that the effective thickness. So, should also take into account the thickness of this top layer the thickness of this particular layer also because how a permeant a let us say.

A is a permeant here it is diffusing once it is diffuse to the top layer then when it comes to the sub layer is a distinct layer this you need to understand that the layers are quite distinct. So, they are how what resistance is being offered to its transport or to it is permeates to this particular layer that will be decided by what is the thickness of the sub layer.

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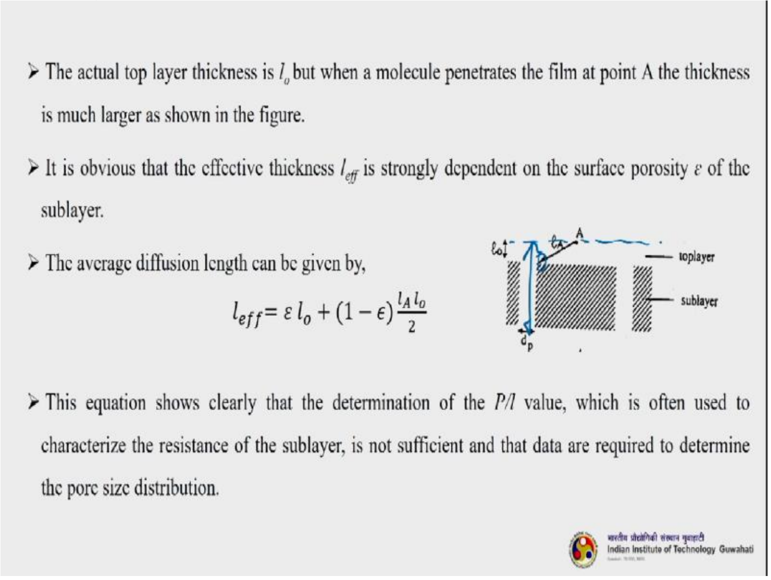

- The actual top layer thickness is l_o but when a molecule penetrates the film at point A the thickness is much larger as shown in the figure.
- It is obvious that the effective thickness l_{eff} is strongly dependent on the surface porosity ε of the sublayer.
- The average diffusion length can be given by,

$$l_{eff} = \varepsilon\, l_o + (1-\varepsilon)\frac{l_A\, l_o}{2}$$

- This equation shows clearly that the determination of the P/l value, which is often used to characterize the resistance of the sublayer, is not sufficient and that data are required to determine the pore size distribution.

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So, the actual top layer thickness is l naught but when a molecule penetrates the film at point A let us say this is a point A when the molecule is getting permeant, the thickness is much larger as shown in the figure. So, the total thickness becomes something like this, this is a top layer, so total thickness becomes something like this, it is obvious that the effective thickness is strongly dependent on the surface porosity of the sub layer.

Now, the average diffusion length can be calculated by this equation l effective equals to this epsilon l naught, l naught is the top layer thickness plus 1 - epsilon l A l naught / 2.Now, this equation shows clearly that the determination of the value P / l which is providing the resistance actually is open to characterize the resistance of the sub layer is not sufficient and that are required to determine the pore size distribution.

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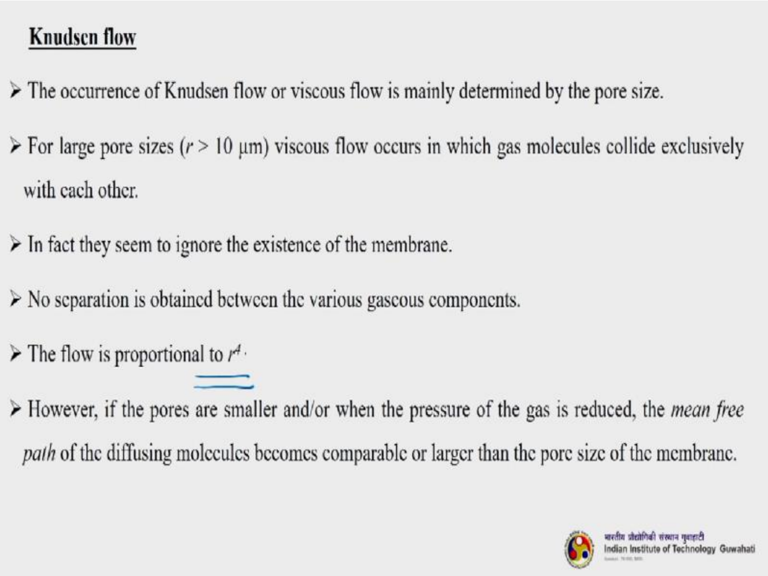

Knudsen flow

- The occurrence of Knudsen flow or viscous flow is mainly determined by the pore size.
- For large pore sizes ($r > 10$ μm) viscous flow occurs in which gas molecules collide exclusively with each other.
- In fact they seem to ignore the existence of the membrane.
- No separation is obtained between the various gaseous components.
- The flow is proportional to r^4.
- However, if the pores are smaller and/or when the pressure of the gas is reduced, the *mean free path* of the diffusing molecules becomes comparable or larger than the pore size of the membrane.

Now, Knudsen flow the occurrence of Knudsen flow or viscous flow is mainly determined by the pore size, let us say for the pores which are up which are largest greater than 10 micron. Viscous flow occurs in which gas molecules collide exclusively with each other. In fact, they seem to ignore the existence of the membrane. No separation is obtained between the viscous gaseous components the flow is proportional to the radiance to the power of 4; here r is the pore radiance.

It is however, if the pores are smaller and or when the pressure of the gas is reduced the mean free path of the diffusing molecules becomes comparable or larger than the pore size of the membrane.

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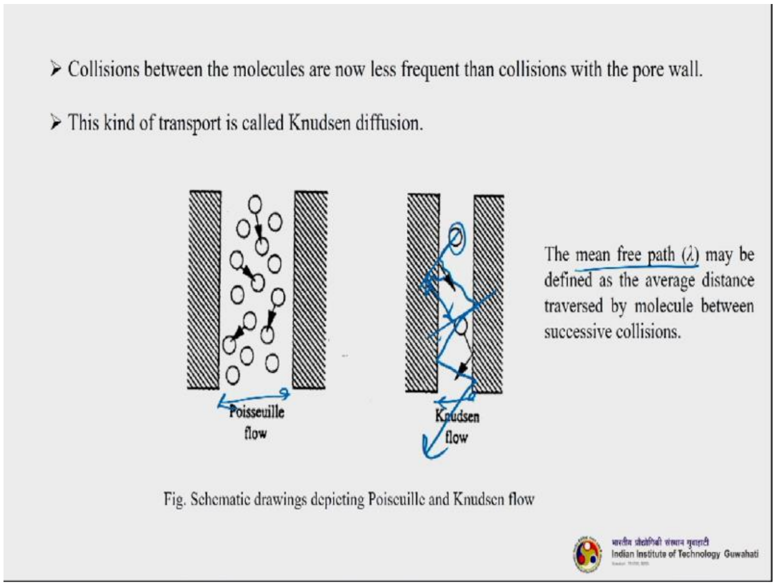

- Collisions between the molecules are now less frequent than collisions with the pore wall.
- This kind of transport is called Knudsen diffusion.

The mean free path (λ) may be defined as the average distance traversed by molecule between successive collisions.

Fig. Schematic drawings depicting Poiseuille and Knudsen flow

Now, let us see the figure actually, so, the collisions between the molecules are now less frequent than the collisions of the pore wall this is what happened. So, in case the pore size this is the pore size you can see the pore size this is bigger than what is happening the Poiseuille flow is happened now here the pore wall is not contributing to anything. Now, when the pore wall come into picture when the pore size decreases you see this pore size decreases it is smaller than this pore size.

So, here the pore wall will have a affect how through the mean free path what is mean free path. The mean free path may be defined as the average distance traversed by molecule between 2 successive collisions this molecule is getting coming here, than it is coming here, again it is coming here, again it is coming, then finally it is coming out. So, we can see the mean free path something like this. So, this is the mean free path. So, mean free path is the distance that is traversed by a particular molecule between 2 successive collisions. So, this is what is mean free path.

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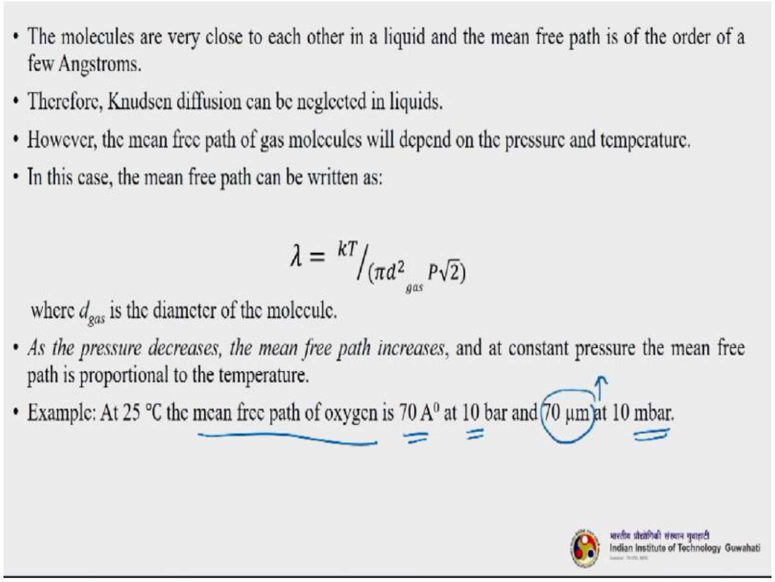

- The molecules are very close to each other in a liquid and the mean free path is of the order of a few Angstroms.
- Therefore, Knudsen diffusion can be neglected in liquids.
- However, the mean free path of gas molecules will depend on the pressure and temperature.
- In this case, the mean free path can be written as:

$$\lambda = {}^{kT}\!/(\pi d^2_{gas} P\sqrt{2})$$

where d_{gas} is the diameter of the molecule.

- *As the pressure decreases, the mean free path increases*, and at constant pressure the mean free path is proportional to the temperature.
- Example: At 25 °C the mean free path of oxygen is 70 A^0 at 10 bar and 70 µm at 10 mbar.

The molecules are very close to each other in a liquid and the mean free path is the order of few angstroms. So, in the liquid actually the mean free path has no practical relevance. So, that is why in liquids Knudsen diffusion is usually neglected. However, in case of gas molecules the mean free path well plays a big role, because it depends on the pressure and temperature. So, for gases we can calculate the mean free path from this particular equation.

So lambda equals to lambda is the mean free path so lambda = KT / pi d gas square p under root 2 where d gas is the diameter of the molecule. Now, you can see this as the pressure decreases the mean free path increases whenever the pressure will decrease the mean free path will increase at constant pressure the mean free path is proportional to the temperature. Now, for an example let us say at 25 degrees centigrade, what is happening the mean free path of oxygen, it is 70 angstrom at 10 bar and what is happening when we are reducing the pressure we reducing the pressure to 10 millibar the mean free path increases from 70 angstroms to 70 micron.

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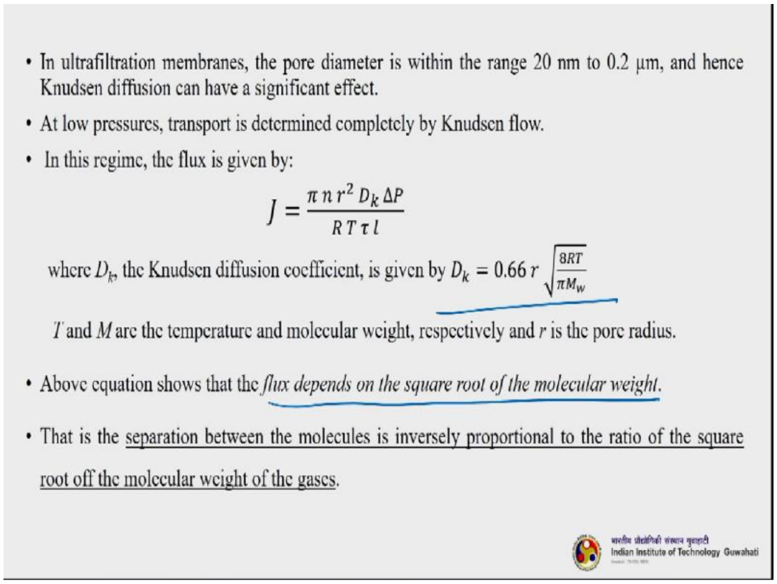

- In ultrafiltration membranes, the pore diameter is within the range 20 nm to 0.2 µm, and hence Knudsen diffusion can have a significant effect.
- At low pressures, transport is determined completely by Knudsen flow.
- In this regime, the flux is given by:

$$J = \frac{\pi\, n\, r^2\, D_k\, \Delta P}{R\, T\, \tau\, l}$$

where D_k, the Knudsen diffusion coefficient, is given by $D_k = 0.66\, r \sqrt{\frac{8RT}{\pi M_w}}$

T and M are the temperature and molecular weight, respectively and r is the pore radius.

- Above equation shows that the *flux depends on the square root of the molecular weight*.
- That is the separation between the molecules is inversely proportional to the ratio of the square root off the molecular weight of the gases.

So, in ultrafiltration membranes the pore diameter is within the range 20 nanometer to point 2 micron and hence Knudsen diffusion can have a significant effect. Now at low pressure transport is determined completely by Knudsen flow. In this regime, the flux is given by this equation J = pi n r square D k delta p / R T tau l. So, here D k is Knudsen diffusion coefficient it is given by this particular equation 0.66 r 8RT divided by pi M w under roots. So, what is M w and M w is the molecular weight of the component.

And T is the temperature and R is the pore radiance now, the above equation is showing clearly the flux depends on the square root of the molecular weight that is that means, the separation between the molecules is inversely proportional to the ratio of the square root of the molecular weight of the gases.

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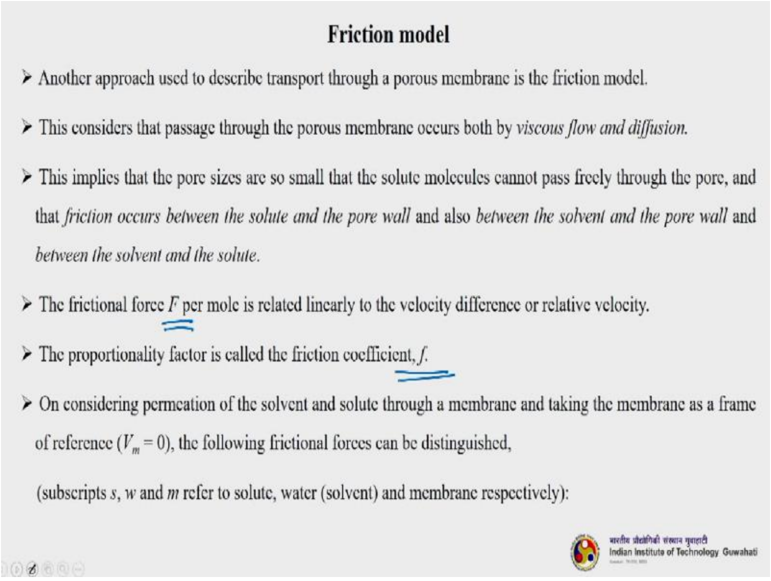

Friction model

- Another approach used to describe transport through a porous membrane is the friction model.
- This considers that passage through the porous membrane occurs both by *viscous flow and diffusion.*
- This implies that the pore sizes are so small that the solute molecules cannot pass freely through the pore, and that *friction occurs between the solute and the pore wall* and also *between the solvent and the pore wall* and *between the solvent and the solute.*
- The frictional force F per mole is related linearly to the velocity difference or relative velocity.
- The proportionality factor is called the friction coefficient, f.
- On considering permeation of the solvent and solute through a membrane and taking the membrane as a frame of reference ($V_m = 0$), the following frictional forces can be distinguished,

  (subscripts s, w and m refer to solute, water (solvent) and membrane respectively):

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So, another approach to describe the transport through membrane is a friction model. Now, what is happening and why this model is coming to picture that because when the pore sizes are small, then the solid molecules cannot pass freely through the pores and what is happening. Now the friction is occurring friction is occurring between what friction is occurring between the solute and the pore wall between the solvent and the pore wall as well as the solvent and the solute.

So, 3 types of frictions are happening between solute pore wall solvent pore wall and solute and solvent. Now, the frictions force F per mole is related linearly to the velocity difference or relative velocity, the proportionality factor is called the friction coefficient f. So, F is the friction force f is that friction coefficient. Now friction model takes into account the passes through the porous membrane, which is occurring both by viscose flow as well as diffusion.

Now on considering permeation of the solvent and solute through a membrane and taking the membrane is a frame of reference, the following frictional process can be distinguished. Now in the next slide I am showing the questions. So the subscript s, w and m refer to the solute water and membrane and respectively.

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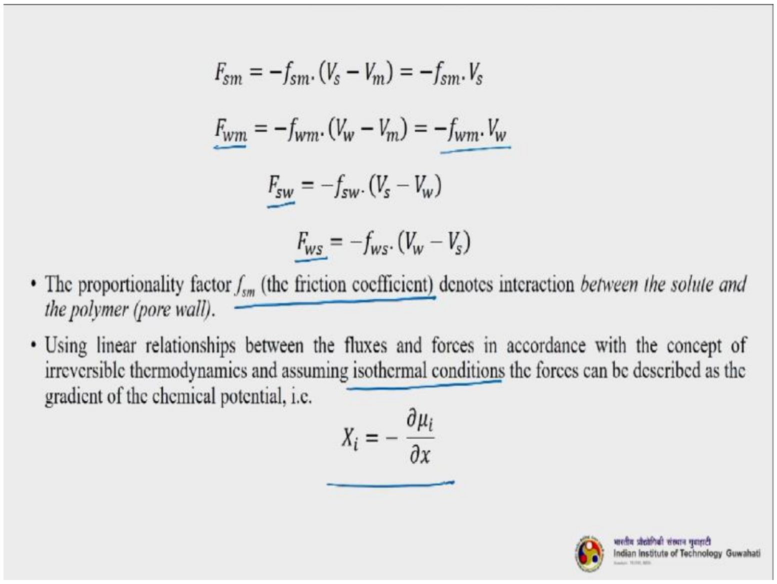

$$F_{sm} = -f_{sm}\cdot(V_s - V_m) = -f_{sm}\cdot V_s$$

$$F_{wm} = -f_{wm}\cdot(V_w - V_m) = -f_{wm}\cdot V_w$$

$$F_{sw} = -f_{sw}\cdot(V_s - V_w)$$

$$F_{ws} = -f_{ws}\cdot(V_w - V_s)$$

- The proportionality factor f_{sm} (the friction coefficient) denotes interaction *between the solute and the polymer (pore wall).*
- Using linear relationships between the fluxes and forces in accordance with the concept of irreversible thermodynamics and assuming isothermal conditions the forces can be described as the gradient of the chemical potential, i.e.

$$X_i = -\frac{\partial \mu_i}{\partial x}$$

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Now F sm that is the frictional pores for solute and membrane between solute and membrane is equal to minus F sm there is the frictional coefficient between solute and membrane V s - V m = - f sm V s. So, here also we have written the equation for F wm. So, the fictional pores between water and membrane can be expressed is that - f wm V w. F sw is another one which is the frictional coefficient denotes interaction between the solute and the water.

And then F ws we can write that here. F ws equals to the friction force between the water and solute is minus F ws V w - V s. Now the proportionality factor F sm which is the frictional coefficient denotes the interaction between the solute and the polymer that is actually m denotes the membrane. So, membrane is the polymer or essentially we can say also pore wall now using linear relationship between fluxes.

And forces in accordance with the concept of irreversible thermal dynamics and assuming isothermal conditions, the process can be described as the gradient of the chemical potential, so, X i = - d mu i / dx. So, we know this we have discussed this many times.

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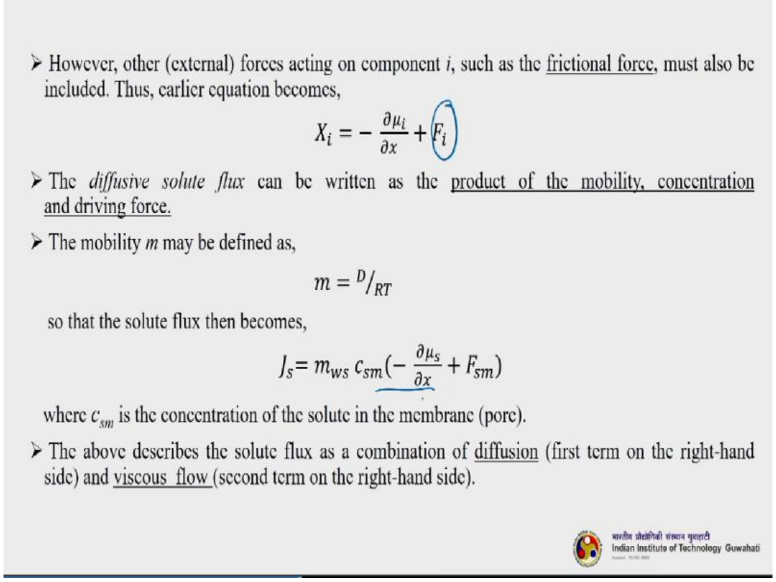

- However, other (external) forces acting on component *i*, such as the frictional force, must also be included. Thus, earlier equation becomes,

$$X_i = -\frac{\partial \mu_i}{\partial x} + \boxed{F_i}$$

- The *diffusive solute flux* can be written as the product of the mobility, concentration and driving force.
- The mobility *m* may be defined as,

$$m = {}^{D}/_{RT}$$

so that the solute flux then becomes,

$$J_s = m_{ws}\, \underline{c_{sm}(-\frac{\partial \mu_s}{\partial x}} + F_{sm})$$

where c_{sm} is the concentration of the solute in the membrane (pore).

- The above describes the solute flux as a combination of diffusion (first term on the right-hand side) and viscous flow (second term on the right-hand side).

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However, other external forces are acting on the component and what are those forces those are conflictnal process. So, we cannot neglect them. So, hence then it needs to be included. So, that equation an earlier equation which is X i = - d mu i / dx this between the flux and the forces so, we can rewrite by adding the component F i the frictional force. Now, the diffusive solid flux can be written as the product of mobility, concentration and driving force.

Now, what is mobility can be expressed as D / RT and the solute flux then becomes J s = m ws C sm - d mew s / dx + F sm. Now, what is C sm here? C sm with a concentration of the solute in the membrane or we can essentially say also pore also. Now, the above equation describes the solute flux is a combination of diffusion and viscous flow. So, the first term on the right hand side you can see, so this is diffusive flow and that is viscous flows.

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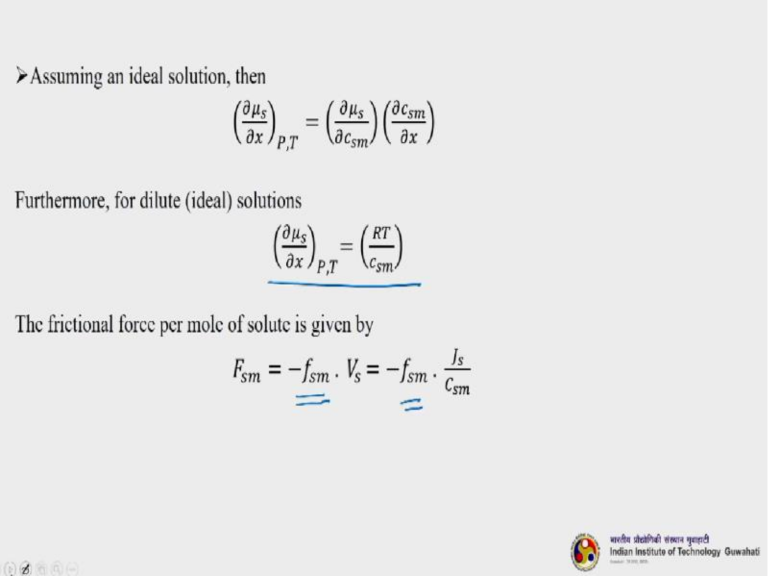

- Assuming an ideal solution, then

$$\left(\frac{\partial \mu_s}{\partial x}\right)_{P,T} = \left(\frac{\partial \mu_s}{\partial c_{sm}}\right)\left(\frac{\partial c_{sm}}{\partial x}\right)$$

Furthermore, for dilute (ideal) solutions

$$\underline{\left(\frac{\partial \mu_s}{\partial x}\right)_{P,T} = \left(\frac{RT}{c_{sm}}\right)}$$

The frictional force per mole of solute is given by

$$F_{sm} = -\underline{f_{sm}} \cdot V_s = -\underline{f_{sm}} \cdot \frac{J_s}{C_{sm}}$$

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Assuming an ideal solution we can write this equation dell mew s / dell x at constant pressure and temperature equals to dell mew s / dell C sm into dell C sm / dell x, Furthermore for dilute ideal solutions we can write this particular request and in terms of dell mew s / dell x = RT / C sm. So, the frictional force per mole of solute is given by F sm is the frictional force between the solute and the membrane equals to - f sm. This is the Frictional coefficient, friction coefficient into V s = - f sm into J s / C sm.

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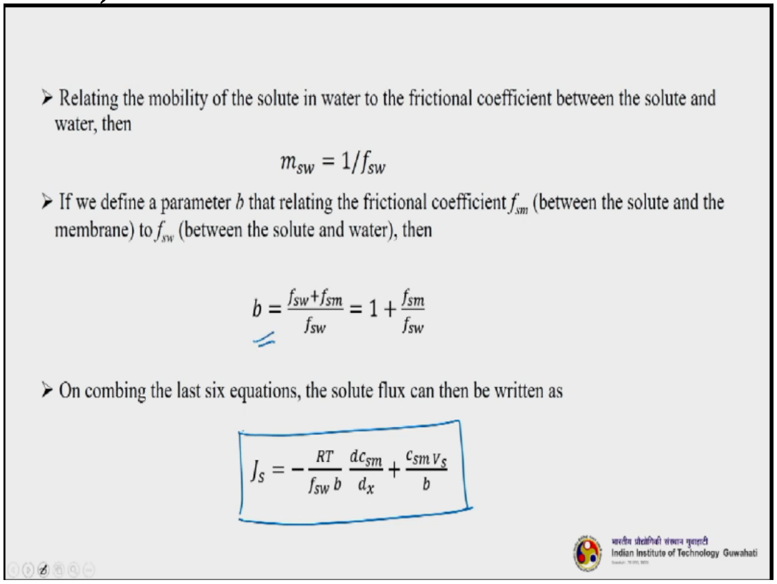

- Relating the mobility of the solute in water to the frictional coefficient between the solute and water, then

$$m_{sw} = 1/f_{sw}$$

- If we define a parameter b that relating the frictional coefficient f_{sm} (between the solute and the membrane) to f_{sw} (between the solute and water), then

$$\underline{b} = \frac{f_{sw}+f_{sm}}{f_{sw}} = 1 + \frac{f_{sm}}{f_{sw}}$$

- On combing the last six equations, the solute flux can then be written as

$$\boxed{J_s = -\frac{RT}{f_{sw}\, b}\frac{dc_{sm}}{d_x} + \frac{c_{sm} v_s}{b}}$$

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Relating the mobility of the solute in water to the frictional coefficient between solute and water then m sw = 1 over f sw. And we define a parameter b that, relating the frictional coefficient that is f sm between the solute and the membrane to a f sw between the solute and water. So we can write that b equals to we are defining a new parameter basically. So, we are defining a new parameter in such a way that the frictional coefficient between the solute and water as well as the solute and the membrane has been taken into account.

So b = f sw + f sm / f sw. So you can write that 1 +f sm / f sw. So I am combining the last 6 equations which we have discussed, we can write the solid flux equals to write in this manner. So J s = - R T / f sw b, then d C sm / dx + C sm V s / b wherever where b is this particular equation.

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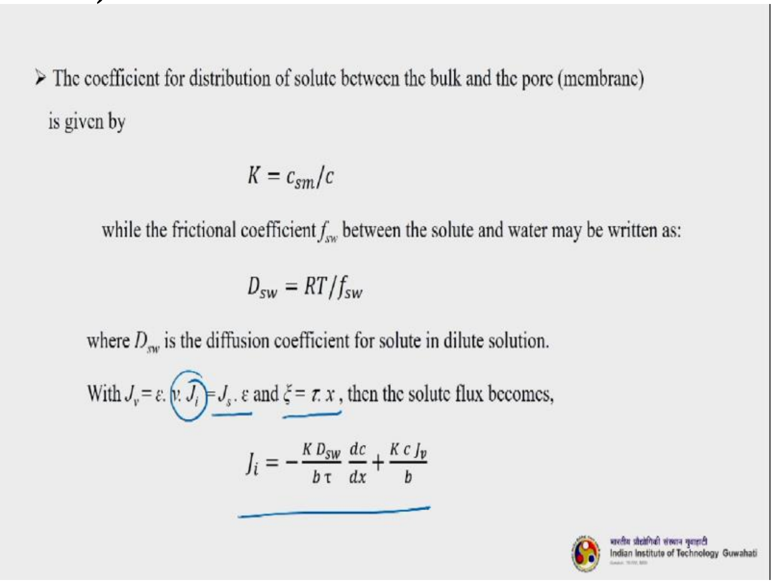

- The coefficient for distribution of solute between the bulk and the pore (membrane) is given by

$$K = c_{sm}/c$$

while the frictional coefficient f_{sw} between the solute and water may be written as:

$$D_{sw} = RT/f_{sw}$$

where D_{sw} is the diffusion coefficient for solute in dilute solution.

With $J_v = \varepsilon.\boxed{v.J_i} = \underline{J_s.\varepsilon}$ and $\underline{\xi = \tau.x}$, then the solute flux becomes,

$$\underline{J_i = -\frac{K\,D_{sw}}{b\,\tau}\frac{dc}{dx} + \frac{K\,c\,J_v}{b}}$$

So, the coefficient for distribution of solute between the bulk and the pore membrane is given by K = C sm / c while the frictional coefficient f sw between the solute and water maybe written as D sw = RT / f sw. So D sw is the diffusion between the solute and the this one water solution and equals to RT / f sw. D sw is the diffusion coefficient for solute in dilute solution, then you can write J v = epsilon v J i and equals to sub flux J s the solid flux into epsilon.

Because v i J i can be written in a J s, then and this is zeta = tau into x then solute flux becomes this, So, writing in terms of J i - K D sw b tau dc / dx + K c J v / b.

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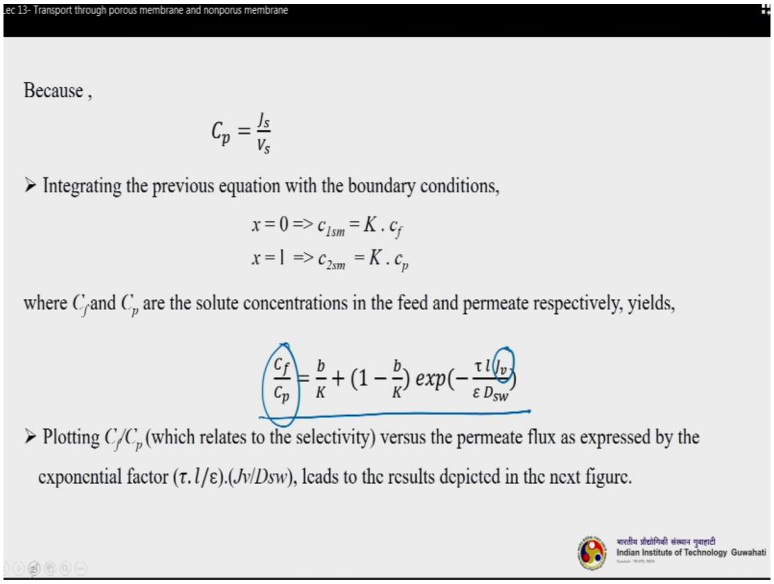

ec 13- Transport through porous membrane and nonporus membrane

Because ,

$$C_p = \frac{J_s}{V_s}$$

- ➤ Integrating the previous equation with the boundary conditions,

$$x = 0 \Rightarrow c_{1sm} = K . c_f$$

$$x = l \Rightarrow c_{2sm} = K . c_p$$

where C_f and C_p are the solute concentrations in the feed and permeate respectively, yields,

$$\underline{\frac{C_f}{C_p} = \frac{b}{K} + (1 - \frac{b}{K})\, exp(-\frac{\tau\, l\, J_v}{\varepsilon\, D_{sw}})}$$

- ➤ Plotting C_f/C_p (which relates to the selectivity) versus the permeate flux as expressed by the exponential factor $(\tau . l/\varepsilon).(Jv/Dsw)$, leads to the results depicted in the next figure.

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Now, since we can express C p = J s / V s. So we can integrate the previous equation with the boundary conditions x = 0 when C 1sm = K into C f, x = 1 that indicates C 2sm = K into C p. But now what is C f and C p, the solute concentrations in the feed and permeate side respectively, Now, once you do that integration we will get this equations C f / C p = b / K + 1 - b / k exponential - tau l J v / epsilon D s w. Now, if you plot C f / C p this C f / C p versus permeate flux J v, as expressed by the exponential factor, so we will see how actually it happens.

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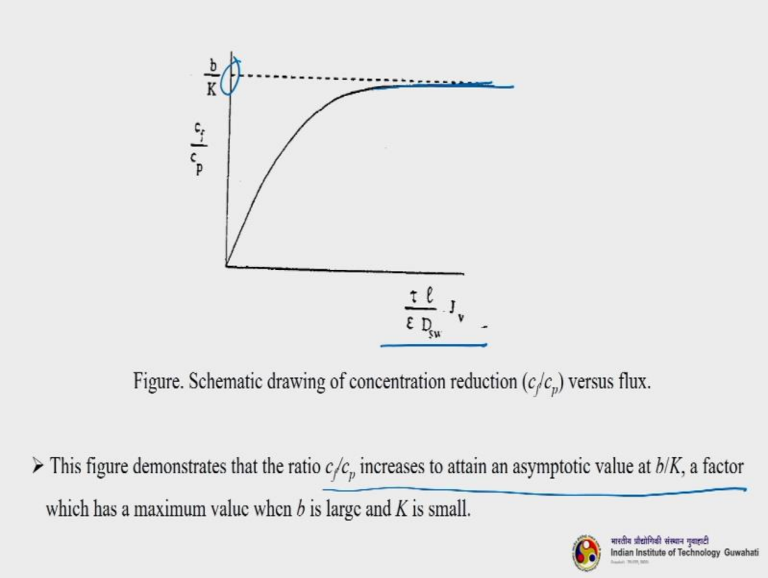

Figure. Schematic drawing of concentration reduction (c_f/c_p) versus flux.

- ➤ This figure demonstrates that the ratio c_f/c_p increases to attain an asymptotic value at b/K, a factor which has a maximum value when b is large and K is small.

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So, you can see this plot actually C f / C p versus this particular permeate flux in which tau l epsilon D sw these are all constant been integrated into that equation. The figure demonstrates that the ratio C f / C p increases to attain asymptotic value at b / K here. So that means is getting saturated here, what is the meaning of that? So, when b is large and K is actually small.

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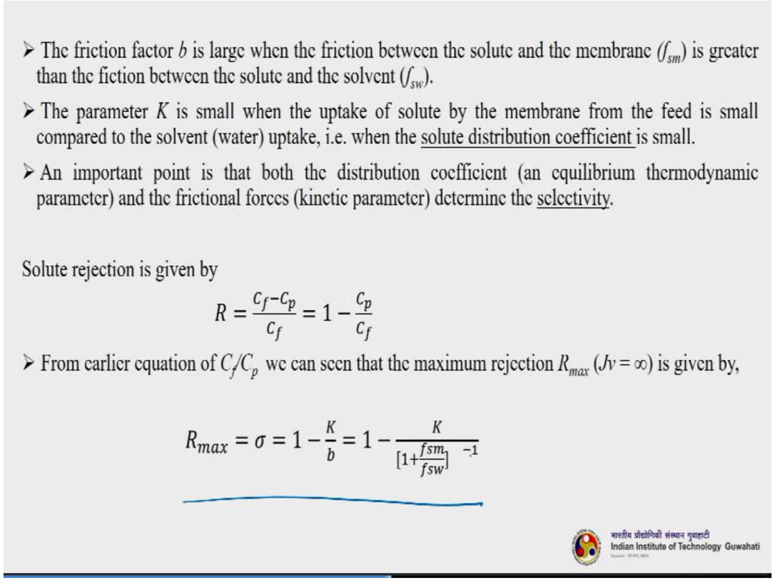

- The friction factor b is large when the friction between the solute and the membrane (f_{sm}) is greater than the fiction between the solute and the solvent (f_{sw}).
- The parameter K is small when the uptake of solute by the membrane from the feed is small compared to the solvent (water) uptake, i.e. when the solute distribution coefficient is small.
- An important point is that both the distribution coefficient (an equilibrium thermodynamic parameter) and the frictional forces (kinetic parameter) determine the selectivity.

Solute rejection is given by

$$R = \frac{C_f - C_p}{C_f} = 1 - \frac{C_p}{C_f}$$

- From earlier equation of C_f/C_p we can seen that the maximum rejection R_{max} ($Jv = \infty$) is given by,

$$R_{max} = \sigma = 1 - \frac{K}{b} = 1 - \frac{K}{[1 + \frac{fsm}{fsw}]^{-1}}$$

So, the friction factor b is large when the friction between the solute and the membrane is greater than the friction between the solute and the solvent, the parameter K is small, when the uptake of the solute by the membrane from the feed is small compared to the solvent water uptake, open the solid distribution cooperation is actually small. An important point is that both distribution coefficient and equilibrium thermodynamic parameter and the frictional forces which is the kinetic parameters determine the selective.

So, students you just noted down, it is very important to remember then the selectivity of the membrane is given by 2 important parameters. The first one is the distribution coefficient, which is actually the equilibrium thermodynamic parameter and the 2nd one is the frictional forces which is arising due to the kinetic parameters. So, both these parameters determines the selectivity.

Now solute rejection can be expressed in terms of C f – C p / C f or 1 – C p / C f the concentration of permeate and concentration C p we have seen that from earlier equation C f / C p we can see that the maximum rejection is happening R max when the J v the volumetric tends to infinity. So, you can write this equation R max = sigma 1- K / b 1 minus this equation this is inverse.

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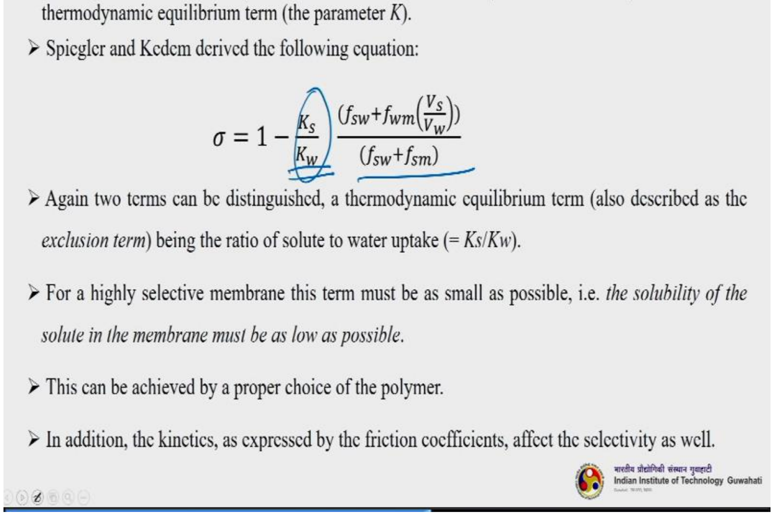

- This equation shows how rejection is related to a kinetic term (the friction factor *b*) and to a thermodynamic equilibrium term (the parameter *K*).
- Spiegler and Kedem derived the following equation:

$$\sigma = 1 - \frac{K_s}{K_w}\frac{\left(f_{sw}+f_{wm}\left(\frac{V_s}{V_w}\right)\right)}{\left(f_{sw}+f_{sm}\right)}$$

- Again two terms can be distinguished, a thermodynamic equilibrium term (also described as the *exclusion term*) being the ratio of solute to water uptake (= *Ks*/*Kw*).
- For a highly selective membrane this term must be as small as possible, i.e. *the solubility of the solute in the membrane must be as low as possible.*
- This can be achieved by a proper choice of the polymer.
- In addition, the kinetics, as expressed by the friction coefficients, affect the selectivity as well.

Now, this equation shows how rejection is related to a kinetic term that is the friction factor b and to a thermodynamic equilibrium term that is the parameter K, Spiegler and Kedem derive the following equation. So, here you can see 2 distinct problems. So, one this is this case K s / K w. So, this is called actually exclusion term. This is the thermodynamic equilibrium term also known as the exclusion term and this term is the another term.

So, for a highly selective membrane this term must be small as small as possible, now, what is the inherent meaning of that now, the solubility of the solute in the membrane should be as much as low possible. So, that is why this tells us K s / K w, this can be how we will achieve this now, this can be achieved by selection of a proper choice of the polymer that is why I told you in maybe our 2nd or 3rd class.

When we are discussing the polymers and the membrane material system that time we have discussed that and what is the importance to study the properties of the membrane material. Let us let us say the polymeric materials we have studied different polymers materials, polyethylene, polypropylene, polytetrafloroethylene pvdf nylon, so many different polystyrene. So, why we have discussed this, because, if you remember recall the term I was telling that the properties of the membrane material plays a big role in most of the membrane.

Separatism it is microfiltration membrane and the pores are usually a very big size. So, in that the membrane material is not playing a big role, but when you go to ultrafiltration and reverse osmosis nanofiltration or non porous membranes then slowly the membrane materials the pore sizes decreases and the membrane material starts playing an important role. So, the membrane material takes part or takes a important role in the separation.

It is very important to understand what is the properties of that particular membrane because depending on that, we can fine tune and choose a particular membrane material to make a membrane which will suit our particular application. So, in addition to the kinetics, friction coefficient and also affect selectivity this we have also discussed into this class also.

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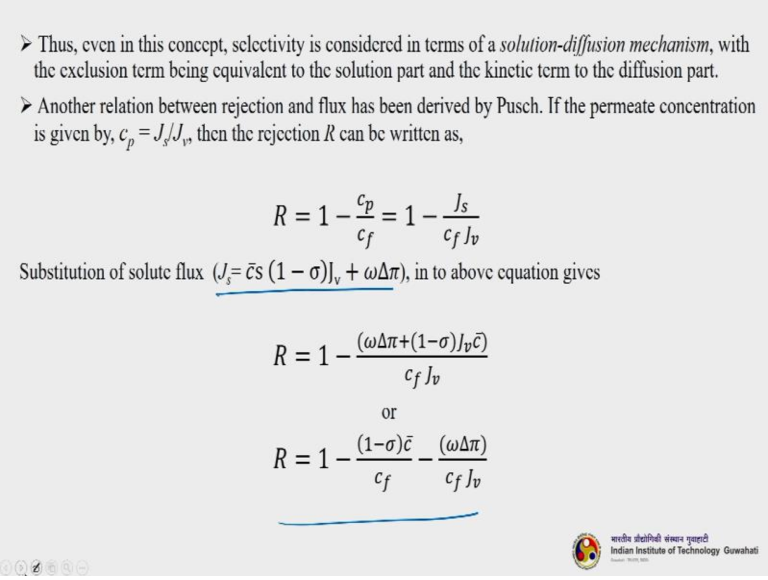

- Thus, even in this concept, selectivity is considered in terms of a *solution-diffusion mechanism*, with the exclusion term being equivalent to the solution part and the kinetic term to the diffusion part.
- Another relation between rejection and flux has been derived by Pusch. If the permeate concentration is given by, $c_p = J_s/J_v$, then the rejection R can be written as,

$$R = 1 - \frac{c_p}{c_f} = 1 - \frac{J_s}{c_f J_v}$$

Substitution of solute flux $(J_s = \bar{c}s\,(1-\sigma)J_v + \omega\Delta\pi)$, in to above equation gives

$$R = 1 - \frac{(\omega\Delta\pi + (1-\sigma)J_v\bar{c})}{c_f J_v}$$

or

$$R = 1 - \frac{(1-\sigma)\bar{c}}{c_f} - \frac{(\omega\Delta\pi)}{c_f J_v}$$

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So, this in this concept selectivity is constant in terms of a solution diffusion mechanism with the exclusion term being equivalent to the solution part and the kinetic term to the diffusion part. So here this particular term is called the exclusion part and this is actually the other term which is the kinetic term to the diffusion part. So another relation between rejection and flux has been derived by Pusch .This if the permeate concentration is given by CP = J s / J v then rejection R can be written as 1 – C p / C f or J s / C f J v.

So, expressing rejection in terms of 2 different fluxes solute flux as well as volume flux substituting the solute flux in this equation this we have discussed earlier. So you can we get R in terms of omega delta pi and J v c f, so here also, or we can just modify this equation and this is just not modification and this is just retained or rearranging the parameters in terms of this reflection coefficient.

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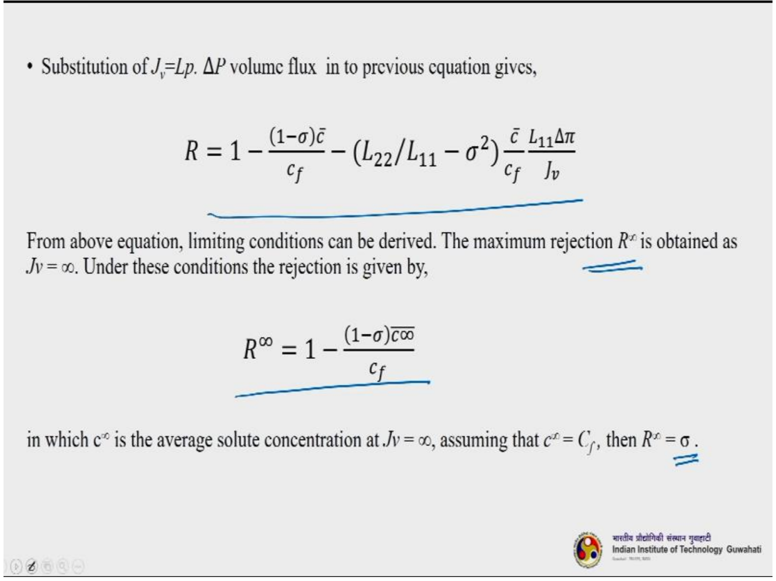

- Substitution of $J_v = Lp.\ \Delta P$ volume flux in to previous equation gives,

$$R = 1 - \frac{(1-\sigma)\bar{c}}{c_f} - (L_{22}/L_{11} - \sigma^2)\frac{\bar{c}}{c_f}\frac{L_{11}\Delta\pi}{J_v}$$

From above equation, limiting conditions can be derived. The maximum rejection R^∞ is obtained as $Jv = \infty$. Under these conditions the rejection is given by,

$$R^\infty = 1 - \frac{(1-\sigma)\overline{c\infty}}{c_f}$$

in which c^∞ is the average solute concentration at $Jv = \infty$, assuming that $c^\infty = C_f$, then $R^\infty = \sigma$.

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So, substituting J v = L p into delta p, that rejection equation becomes something like this. Now here L 22 to L 11comes into picture that reflects them the coupling coefficients as well as the reflection coefficient. Now, from this above equation limiting conditions can be derived, how another maximum rejection that is R infinity is obtained when, your volumetric flux tends to infinity.

So, J v tends to infinity, so, here R infinity or maximum it is external equals to 1 - one sigma c infinity bar / c f now here c infinity is the average solute concentration at J v = infinity, assuming that c infinity = C f and then R infinity = sigma this reflection coefficient.

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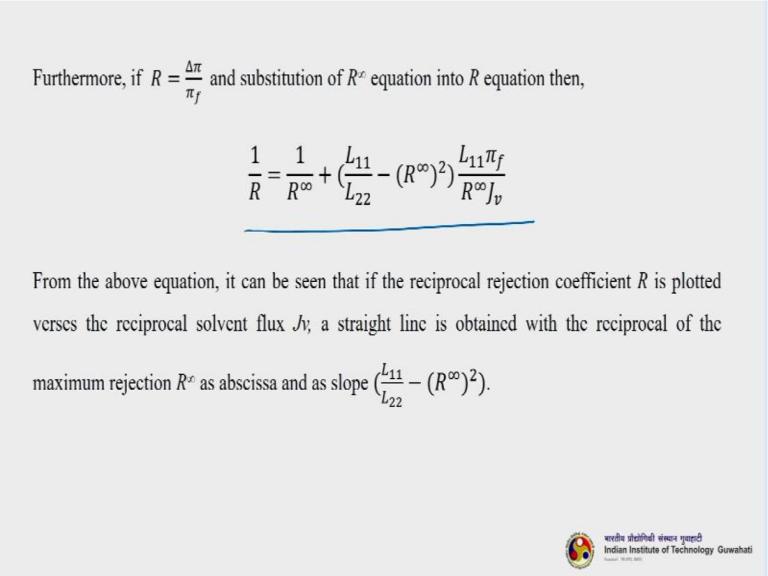

Furthermore, if $R = \frac{\Delta\pi}{\pi_f}$ and substitution of R^{∞} equation into R equation then,

$$\frac{1}{R} = \frac{1}{R^{\infty}} + (\frac{L_{11}}{L_{22}} - (R^{\infty})^2)\frac{L_{11}\pi_f}{R^{\infty}J_v}$$

From the above equation, it can be seen that if the reciprocal rejection coefficient R is plotted verses the reciprocal solvent flux Jv, a straight line is obtained with the reciprocal of the maximum rejection R^{∞} as abscissa and as slope $(\frac{L_{11}}{L_{22}} - (R^{\infty})^2)$.

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Furthermore, if you can express R rejection in terms of aspartic pressure delta pi / delta f substituting R infinity into the above equation you get 1 / R = 1 / R infinity minus this particular equation. Now here are from this equation, we can see that the reciprocal of the rejection coefficient R is plotted versus the reciprocal of the solvent plus J v a straight line is obtained with the reciprocal of the maximum rejection R infinity as the abscissa and this is the slope.

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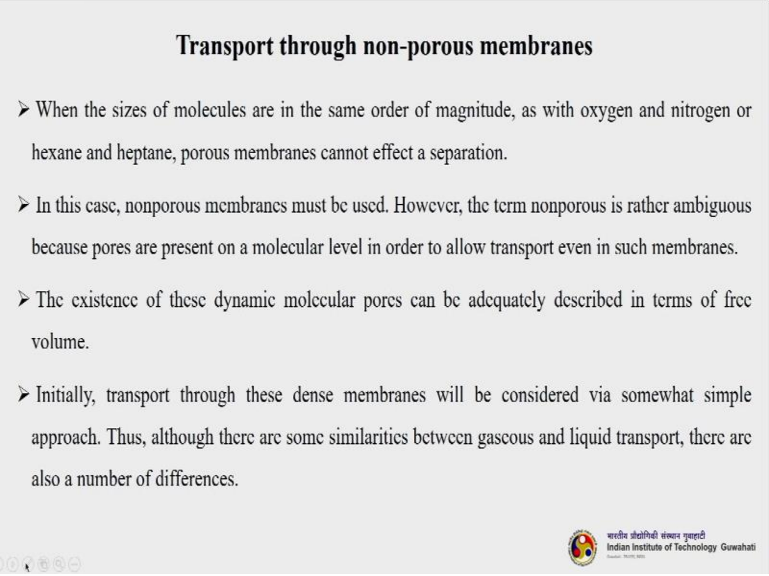

Transport through non-porous membranes

- When the sizes of molecules are in the same order of magnitude, as with oxygen and nitrogen or hexane and heptane, porous membranes cannot effect a separation.
- In this case, nonporous membranes must be used. However, the term nonporous is rather ambiguous because pores are present on a molecular level in order to allow transport even in such membranes.
- The existence of these dynamic molecular pores can be adequately described in terms of free volume.
- Initially, transport through these dense membranes will be considered via somewhat simple approach. Thus, although there are some similarities between gaseous and liquid transport, there are also a number of differences.

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So, let us now discuss the transport through the non porous membrane. Now, when the sizes of molecules are in the same order of magnitude as with oxygen and nitrogen or hexane and heptane porous membranes cannot effect a separation. Now, in this case, non porous membrane must be used. However, the term non porous is rather ambiguous because pores are present on a molecular level in order to allow transport even in such membranes.

Now, the existence of these dynamic molecular pores can be adequately described in terms of free volume. Initially transport through these dense membranes will be considered via somewhat simple approach. Thus although there are some similarities between gaseous and liquid transport, there are also a number of differences.

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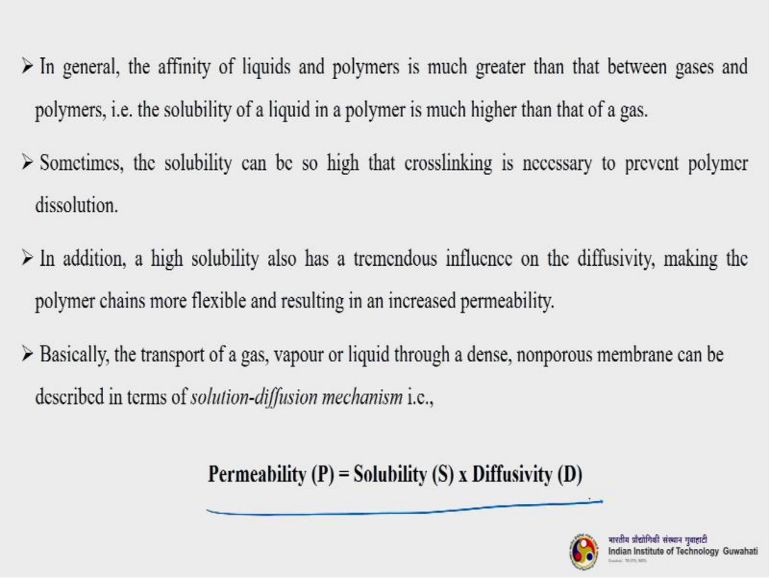

- In general, the affinity of liquids and polymers is much greater than that between gases and polymers, i.e. the solubility of a liquid in a polymer is much higher than that of a gas.
- Sometimes, the solubility can be so high that crosslinking is necessary to prevent polymer dissolution.
- In addition, a high solubility also has a tremendous influence on the diffusivity, making the polymer chains more flexible and resulting in an increased permeability.
- Basically, the transport of a gas, vapour or liquid through a dense, nonporous membrane can be described in terms of *solution-diffusion mechanism* i.e.,

Permeability (P) = Solubility (S) x Diffusivity (D)

So, in general, the affinity of liquids and polymers is much greater than between that gases and polymers, what is the meaning of that term meaning of that the solubility of liquid in a polymer is much higher than that of a gas. So, sometimes the solubility can be so high that cross linking is necessary to prevent polymer dissolution. In addition, a high solubility also has a tremendous influence on the diffusivity making the polymer chains more flexible and resulting in an increased permeability.

Basically, the transport of a gas vapour or liquid through a dense non porous membrane can be described in terms of solution diffusion mechanism. So, here we define permeability equals to solubility in diffusivity.

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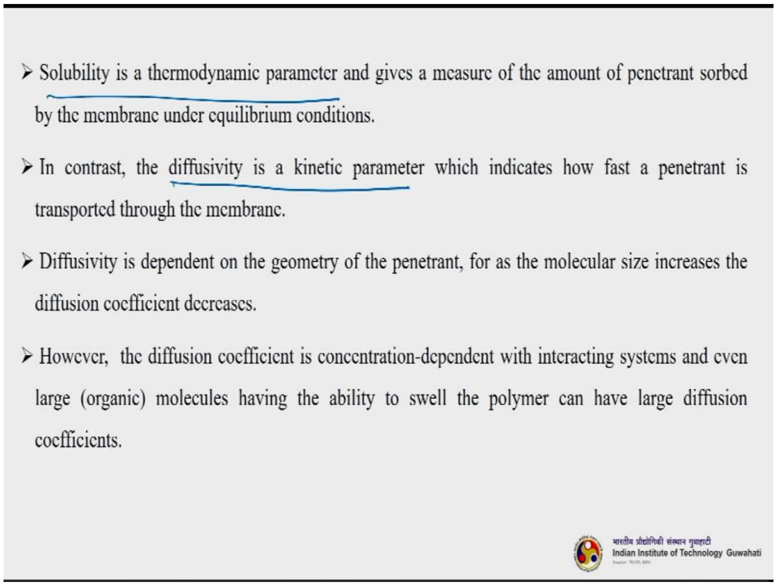

- Solubility is a thermodynamic parameter and gives a measure of the amount of penetrant sorbed by the membrane under equilibrium conditions.
- In contrast, the diffusivity is a kinetic parameter which indicates how fast a penetrant is transported through the membrane.
- Diffusivity is dependent on the geometry of the penetrant, for as the molecular size increases the diffusion coefficient decreases.
- However, the diffusion coefficient is concentration-dependent with interacting systems and even large (organic) molecules having the ability to swell the polymer can have large diffusion coefficients.

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So, solubility is a thermodynamic parameter and it gives a measure of the amount of penetrant served by the membrane under equilibrium conditions in contrast, the diffusivity is a kinetic parameter. So, diffusivity is a kinetic parameter which is solubility a thermodynamic parameter and diffusivity is a kinetic parameter it indicates that how fast a permeant is transported through the membrane.

So, it depends on its diffusion or diffusivity so diffusion constant diffusivity to diffusivity is dependent on the geometry of the penetrant for as the molecular size increases, the diffusion coefficient also decreases. However, diffusion coefficient is a concentration dependent within directing systems and even large organic molecules especially the organic molecules having the ability to swell the polymer can have large diffusion coefficient.

So, the problem is again in the systems of polymeric membrane is that if you are employing organic molecule organic solvents? Then organic solvents will tend to swell the membrane material and what will happen, the pore sizes will increase. So, when the separation is happening this also happen depending upon what is the residence time. So, in that case we last diffusion coefficients will come into picture.

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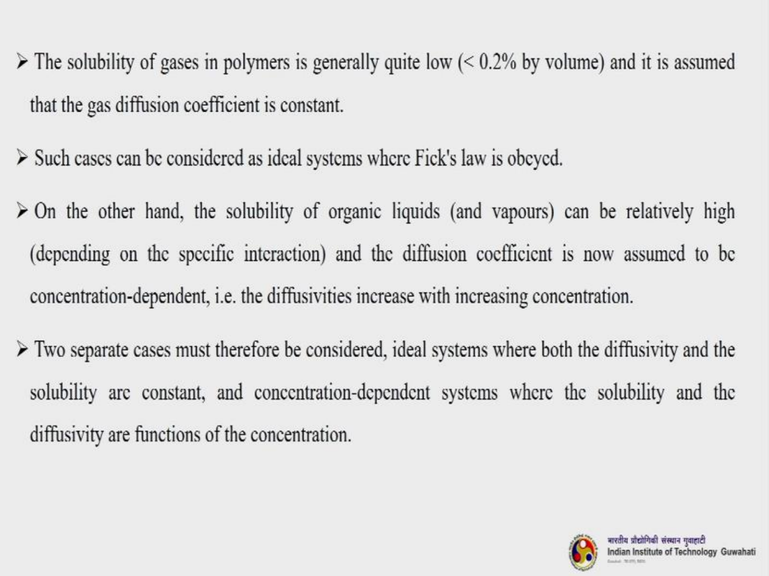

- The solubility of gases in polymers is generally quite low (< 0.2% by volume) and it is assumed that the gas diffusion coefficient is constant.
- Such cases can be considered as ideal systems where Fick's law is obeyed.
- On the other hand, the solubility of organic liquids (and vapours) can be relatively high (depending on the specific interaction) and the diffusion coefficient is now assumed to be concentration-dependent, i.e. the diffusivities increase with increasing concentration.
- Two separate cases must therefore be considered, ideal systems where both the diffusivity and the solubility are constant, and concentration-dependent systems where the solubility and the diffusivity are functions of the concentration.

The solubility of gases in polymers is very low usually point 2% by volume and it is assumed that the gas diffusion coefficient is constant. Now, such cases can be considered as ideal system where Fick’s law is obeyed. On the other hand solubility of organic liquids and vapours can be relatively high depending upon the specific interaction and the diffusion coefficient is now assumed to be concentration dependent that is the diffusivities increase with increasing concentration.

2 separate cases must therefore, be considered ideal systems where both the diffusivity and the solubility are constant and a concentration dependent system or the solubility and diffusivity or functions of the concentration. So, we will discuss these 2 things.

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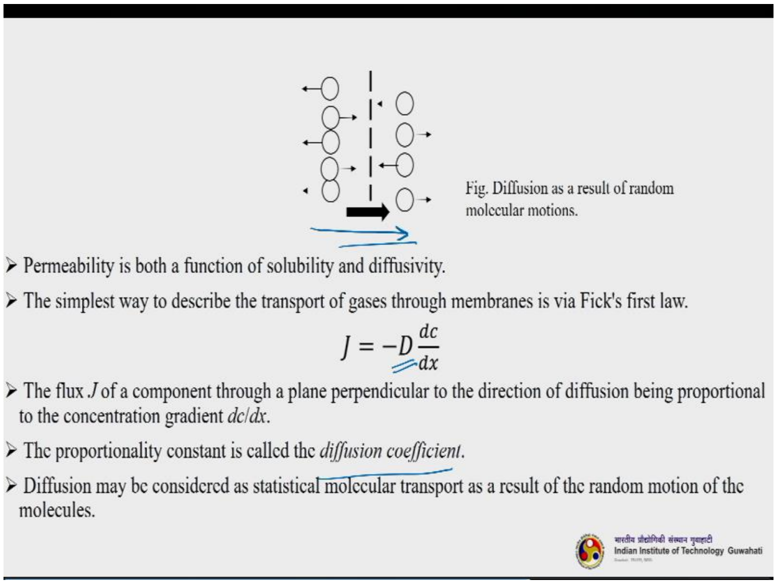

Fig. Diffusion as a result of random molecular motions.

- Permeability is both a function of solubility and diffusivity.
- The simplest way to describe the transport of gases through membranes is via Fick's first law.

$$J = -D\frac{dc}{dx}$$

- The flux *J* of a component through a plane perpendicular to the direction of diffusion being proportional to the concentration gradient *dc*/*dx*.
- The proportionality constant is called the *diffusion coefficient*.
- Diffusion may be considered as statistical molecular transport as a result of the random motion of the molecules.

So, permeability is both a function of solubility and diffusivity the simplest way is to describe the transport of gases is using the Fick’s law J = - D dc / dx, the flux J of a component through a plane perpendicular to the direction of diffusion being proportional to the concentration gradient dc / dx. The proportionality constant is called the diffusion coefficient, this so diffusion may be considered a statistical molecule transport as a result of random motion of the molecules.

So, this is how actually you can see in this figure transport is occurring from this direction to this direction and that random motions of the molecules is happening in both sides upstream side and downstream side of the membrane.

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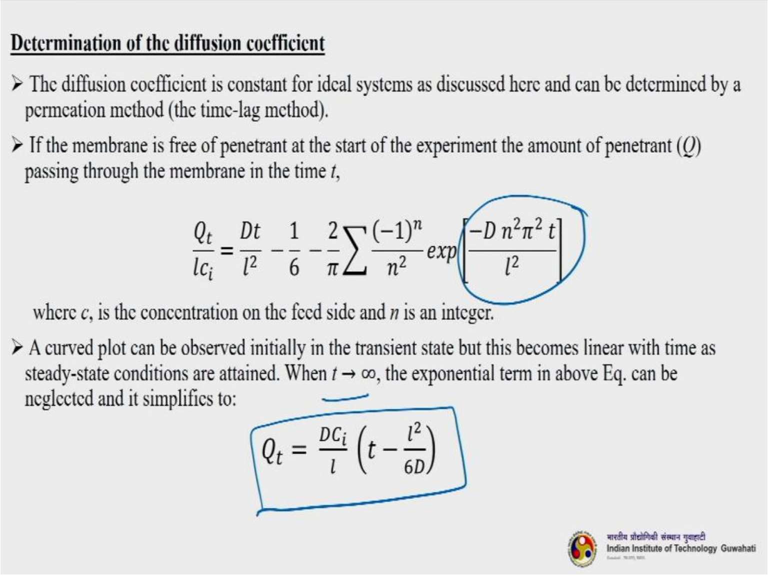

Determination of the diffusion coefficient

- The diffusion coefficient is constant for ideal systems as discussed here and can be determined by a permeation method (the time-lag method).
- If the membrane is free of penetrant at the start of the experiment the amount of penetrant (*Q*) passing through the membrane in the time *t*,

$$\frac{Q_t}{lc_i} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi}\sum\frac{(-1)^n}{n^2}exp\left[\frac{-D\,n^2\pi^2\,t}{l^2}\right]$$

where *c*, is the concentration on the feed side and *n* is an integer.

- A curved plot can be observed initially in the transient state but this becomes linear with time as steady-state conditions are attained. When *t* → ∞, the exponential term in above Eq. can be neglected and it simplifies to:

$$\boxed{Q_t = \frac{DC_i}{l}\left(t - \frac{l^2}{6D}\right)}$$

So, how do we determine the diffusion coefficient, the diffusion coefficient is constant for ideal systems as discussed here and can be determined by a permeation method which is also called is a time lag method. Now, if the membrane is free of penetrant at the start of the experiment the amount of penetrant passing through the membrane in the time t can be calculated. So, this is the equation here c is a concentration on the feed side and n is an integer.

A curved plot can also be observed initially in the transient state, but this becomes linear with time as steady state conditions are attained. So, when t tends to infinity the exponential term of the above equation this can be neglected and it simplifies this, so, the Q t. So, that means, what is this? So, the amount of penetrant that is passing through the membrane at time t is DC i / l into t - l square / 60.

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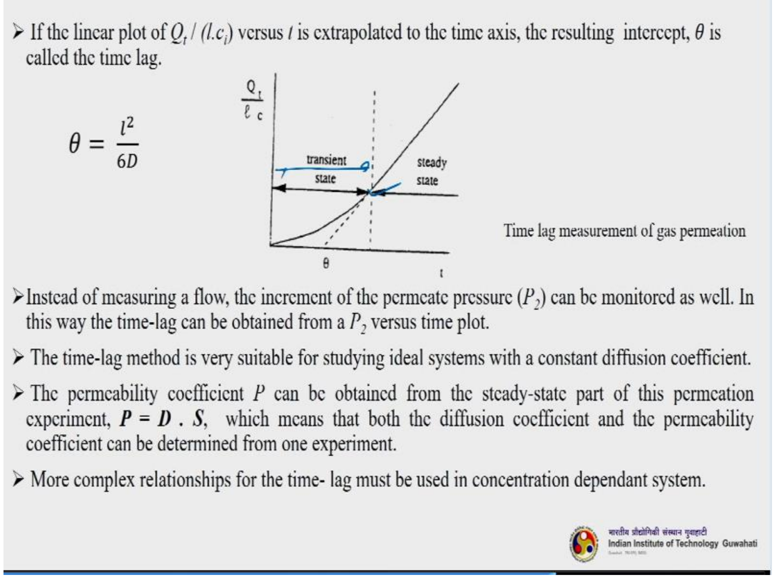

- If the linear plot of $Q_t / (l.c_i)$ versus t is extrapolated to the time axis, the resulting intercept, θ is called the time lag.

$$\theta = \frac{l^2}{6D}$$

Time lag measurement of gas permeation

- Instead of measuring a flow, the increment of the permeate pressure (P_2) can be monitored as well. In this way the time-lag can be obtained from a P_2 versus time plot.
- The time-lag method is very suitable for studying ideal systems with a constant diffusion coefficient.
- The permeability coefficient P can be obtained from the steady-state part of this permeation experiment, $\boldsymbol{P = D \,.\, S}$, which means that both the diffusion coefficient and the permeability coefficient can be determined from one experiment.
- More complex relationships for the time- lag must be used in concentration dependant system.

So, if the linear plot of Q t per l C i versus t is extrapolated to the time axis, the resulting intercept theta is called the time lag. So, theta = l square / 60. So, you can see this from this particular figure which is actually extra plot. So, you can see this is actually the transient state from here to here and that steady state begins from here onwards. And, instead of measuring a flow the increment of the permeate pressure.

Can be monitored as well in this way the time lag can be obtained from a P 2 versus time plot, the time lag method is very suitable for studying ideal systems with a constant diffusion coefficient, the permeability coefficient P can be obtained from the steady state part of this permeation coefficient, which means that both diffusion coefficient and permeability coefficient can be determined from one experiment.

So, this is the most important understanding that we can calculate both at the diffusion coefficient as permeability coefficient from one particular equation provided we know either D or S. So, more complex relationship or the time left must be used in concentration dependent system.

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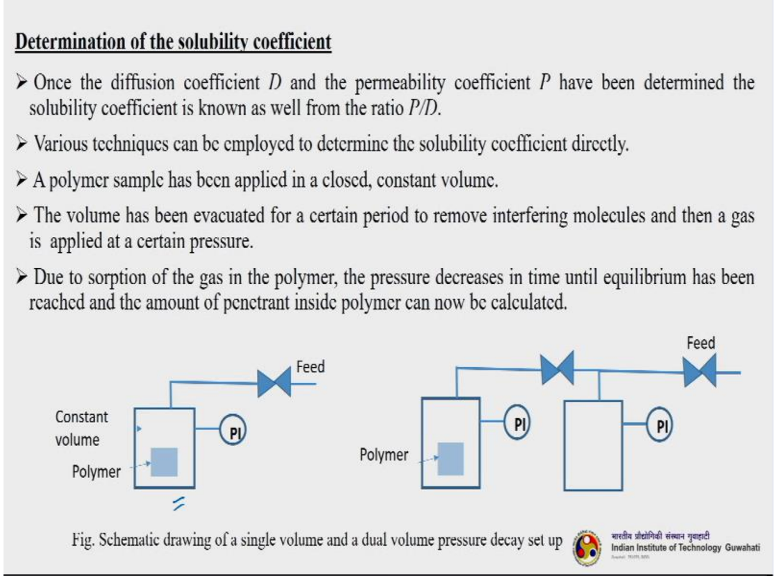

Determination of the solubility coefficient

- Once the diffusion coefficient *D* and the permeability coefficient *P* have been determined the solubility coefficient is known as well from the ratio *P/D*.
- Various techniques can be employed to determine the solubility coefficient directly.
- A polymer sample has been applied in a closed, constant volume.
- The volume has been evacuated for a certain period to remove interfering molecules and then a gas is applied at a certain pressure.
- Due to sorption of the gas in the polymer, the pressure decreases in time until equilibrium has been reached and the amount of penetrant inside polymer can now be calculated.

Fig. Schematic drawing of a single volume and a dual volume pressure decay set up

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And now, we understand how do we calculate or determine the solubility coefficient. Now, once the diffusion coefficient and the permeability coefficient have been determined the solubility coefficient is also can be calculated from the ration P / D. Now, various techniques can be employed to determine the solubility coefficient directly or experimentally, a polymer sample has been applied in a closed constant volume here just like you can see this.

It is a constant volume system or reactor in which the polymer sample is applied, the volume has been evacuated for a certain period to remove interfering molecules and then the gas is applied at a certain pressure due to absorption of the gas in the polymer the pressure decreases in time until the equilibrium has been reached, since the gas will start to so what is happening initially is that so, there is reactor you can understand the chamber in which the polymer sample is kept, and then it is basically evacuated, once it is done, then we pass a particular gas.

So and this gas will start to deserve on the observe the surface of the polymer sample now, the pressure will start decreasing their way that that is where the pressure will start decreasing until equilibrium has been reached. So, that means that will be no more sorption of the gas on the polymer surface and the amount of penetrant inside polymer can now be calculated very easily because we know how much gas we have the volume of gases that is being supplied inside the chamber is being known to us.

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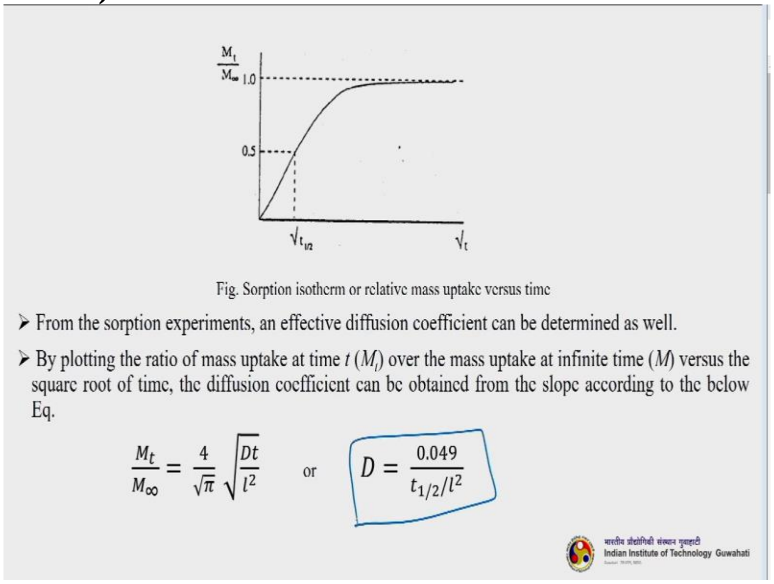

Fig. Sorption isotherm or relative mass uptake versus time

- From the sorption experiments, an effective diffusion coefficient can be determined as well.
- By plotting the ratio of mass uptake at time *t* (M_t) over the mass uptake at infinite time (M) versus the square root of time, the diffusion coefficient can be obtained from the slope according to the below Eq.

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}}\sqrt{\frac{Dt}{l^2}} \quad \text{or} \quad \boxed{D = \frac{0.049}{t_{1/2}/l^2}}$$

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So, from the sorption experiments, an effective diffusion coefficient can be determined as well as, so, by plotting the ratio of mass uptake at time t about the mass uptake at infinite time versus the square root of the time that diffusion coefficient can be obtained. So, we can get diffusion coefficient from this equation D = 0.049 t half / l square.

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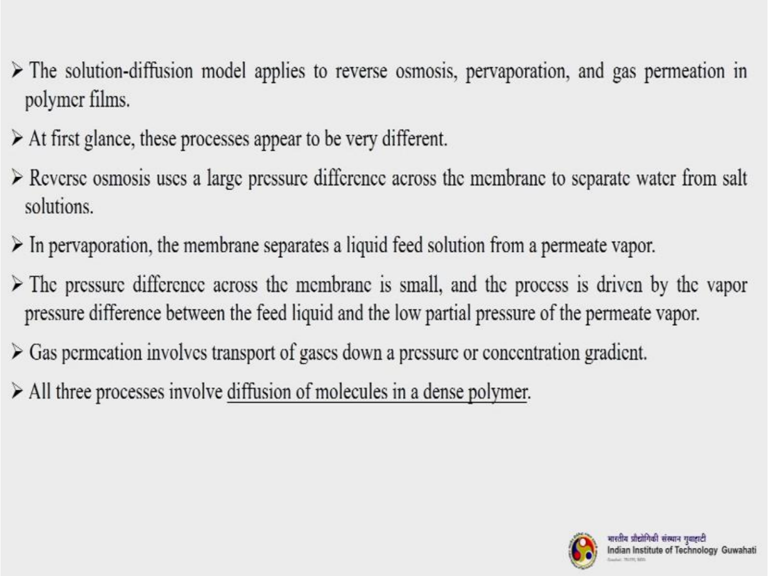

- The solution-diffusion model applies to reverse osmosis, pervaporation, and gas permeation in polymer films.
- At first glance, these processes appear to be very different.
- Reverse osmosis uses a large pressure difference across the membrane to separate water from salt solutions.
- In pervaporation, the membrane separates a liquid feed solution from a permeate vapor.
- The pressure difference across the membrane is small, and the process is driven by the vapor pressure difference between the feed liquid and the low partial pressure of the permeate vapor.
- Gas permeation involves transport of gases down a pressure or concentration gradient.
- All three processes involve diffusion of molecules in a dense polymer.

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The solution diffusion model applies to reverse osmosis pervaporation and gas permeation in polymer films at first glance, this processes appears to be very different reverse osmosis. Why? Because reverse osmosis uses large pressure difference across the membrane and to separate water from salt solutions. In pervaporation usually the membrane separates a liquid feed solution from a permeate vapor.

The pressure difference across the membrane is small and the process is driven by the vapor pressure difference between the feed liquid and the low partial pressure of the permeate vapor so the gas permeation involves transport of gases down the pressure or concentration gradient. All 3 processes involve diffusion of molecules in a dense polymeric membrane.

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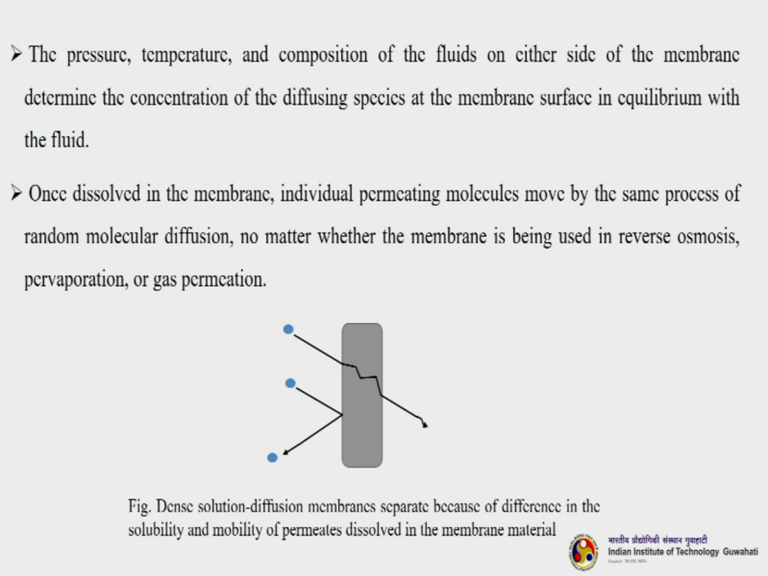

- The pressure, temperature, and composition of the fluids on either side of the membrane determine the concentration of the diffusing species at the membrane surface in equilibrium with the fluid.
- Once dissolved in the membrane, individual permeating molecules move by the same process of random molecular diffusion, no matter whether the membrane is being used in reverse osmosis, pervaporation, or gas permeation.

Fig. Dense solution-diffusion membranes separate because of difference in the solubility and mobility of permeates dissolved in the membrane material

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The pressure temperature and composition of the fluids on either side of the membrane determine the concentration of the diffusing species at the membrane surface in equilibrium with the feed. Now once deserved in the membrane, individual permeating molecules move by the same process of random molecular diffusion, no matter whether the membrane is being used in the reverse osmosis pervaporation gas permeation.

So this is how actually a dense solution diffusion membrane separate from because of differences in the solubility and the mobility of the permeats dissolved in the membrane material.

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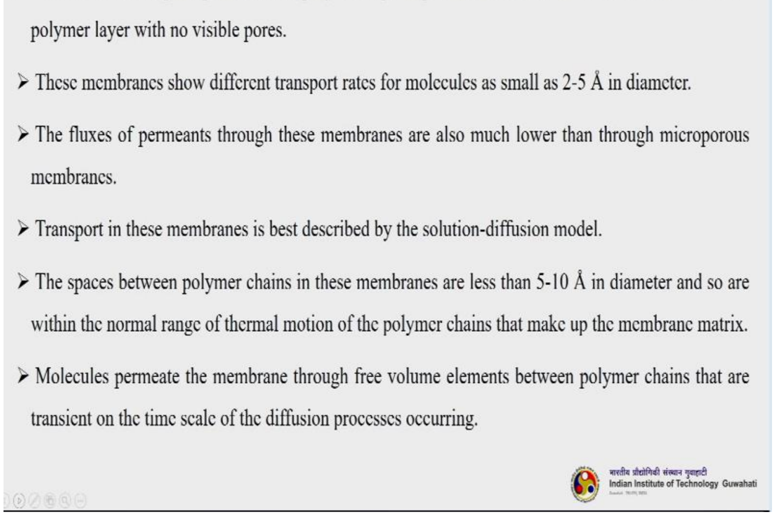

- Reverse osmosis, pervaporation, and polymeric gas separation membranes contain a dense selective polymer layer with no visible pores.
- These membranes show different transport rates for molecules as small as 2-5 Å in diameter.
- The fluxes of permeants through these membranes are also much lower than through microporous membranes.
- Transport in these membranes is best described by the solution-diffusion model.
- The spaces between polymer chains in these membranes are less than 5-10 Å in diameter and so are within the normal range of thermal motion of the polymer chains that make up the membrane matrix.
- Molecules permeate the membrane through free volume elements between polymer chains that are transient on the time scale of the diffusion processes occurring.

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Reverse osmosis pervaporation and polymeric gas separation membranes contain a dense selective polymer layer with no visible pores that is on the top layer. These membranes are different transport rates molecules as small as 2 to 5 angstrom in diameter, and the flux of permeants through these membranes are also much lower than through the micro porous membrane.

Transport in these membranes is best described by the solution diffusion model. The spaces between polymer chains in these membranes are less than 5 to 10 angstrom in diameter, and so are within the normal range of the thermal motion of the polymer chain that makes up the membrane metrics. Actually very small molecules small size of the molecules can permeate through this non porous membrane. The molecules permeate the membrane through free volume elements between polymer chains that are transient and timescale of the diffusion process that is occurring.

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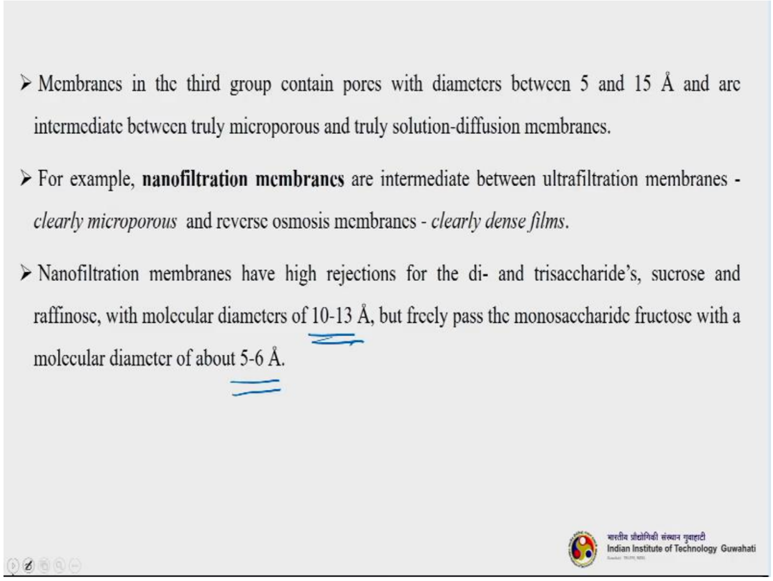

- Membranes in the third group contain pores with diameters between 5 and 15 Å and are intermediate between truly microporous and truly solution-diffusion membranes.
- For example, **nanofiltration membranes** are intermediate between ultrafiltration membranes - *clearly microporous* and reverse osmosis membranes - *clearly dense films*.
- Nanofiltration membranes have high rejections for the di- and trisaccharide's, sucrose and raffinose, with molecular diameters of 10-13 Å, but freely pass the monosaccharide fructose with a molecular diameter of about 5-6 Å.

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And membranes in the 3rd group contain pores with a diameter between 5 and 15 armstrung and are intermediate between truly micro porous and truly solution diffusion membranes. So, these are some transition arrangements you can say that for example, the classic example is the NF membranes, now nanofiltration membranes. So, they are intermediate between the UF membranes, which are clearly micro porous and the reverse osmosis membrane which is clearly dense films.

So, NF is something between a porous membrane and a non porous membrane. So, nanofiltration membranes have high rejections for the di and trisaccharide's for example sucrose and raffinose with molecular diameter of 10 to 13 armstrung but freely pass the monosaccharide frutos with a molecular diameter of 5 to 6. So, you can understand that the diameter of the molecule the size that plays an important role, and eventually the membrane material on the top layer membrane material will determines the separation or the separation efficiency.

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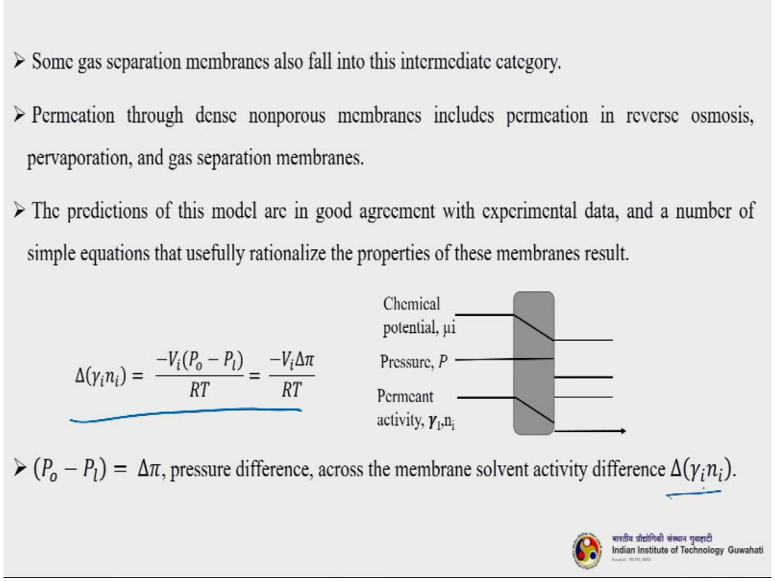

- Some gas separation membranes also fall into this intermediate category.
- Permeation through dense nonporous membranes includes permeation in reverse osmosis, pervaporation, and gas separation membranes.
- The predictions of this model are in good agreement with experimental data, and a number of simple equations that usefully rationalize the properties of these membranes result.

$$\underline{\Delta(\gamma_i n_i) = \frac{-V_i(P_o - P_l)}{RT} = \frac{-V_i \Delta\pi}{RT}}$$

- $(P_o - P_l) = \Delta\pi$, pressure difference, across the membrane solvent activity difference $\underline{\Delta(\gamma_i n_i)}$.

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Some gas separation membrane also fall into this intermediate category. Now permeation through dense non porous membranes includes permeation in reverse osmosis pervaportion and gas separation. Now the predictions of this model are in good agreement with the experimental data and the number of simple equations that usually rationalize the properties of these membranes result.

So, you can write this equation in terms of activity coefficient. So, these are beings on the gradient actually chemical potential pressure the polymer activity. So, we can write P naught - P l = Delta pi expressing in terms of the osmotic pressure and the difference across the membranes also solvent activity difference, the activity coefficient.

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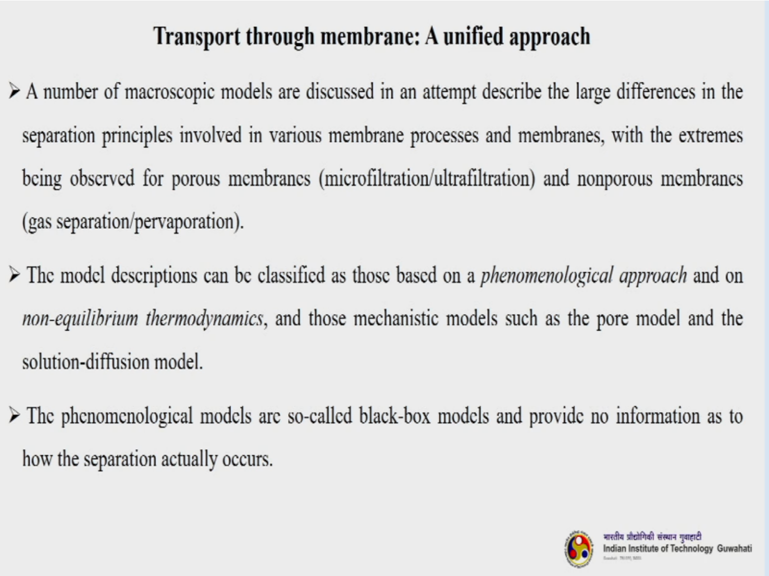

Transport through membrane: A unified approach

- A number of macroscopic models are discussed in an attempt describe the large differences in the separation principles involved in various membrane processes and membranes, with the extremes being observed for porous membranes (microfiltration/ultrafiltration) and nonporous membranes (gas separation/pervaporation).
- The model descriptions can be classified as those based on a *phenomenological approach* and on *non-equilibrium thermodynamics*, and those mechanistic models such as the pore model and the solution-diffusion model.
- The phenomenological models are so-called black-box models and provide no information as to how the separation actually occurs.

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A number of macroscopic models are discussed in an attempt to describe the large differences in the separation principles, involved in various membrane processes and membranes, with the extremes being observed for porous membranes and non porous membranes. The model description can be classified as those based on a phenomenological approach and a non equilibrium thermodynamics.

So, those mechanistic models such as the pore model and the solution, diffusion model will be taken into account. Now, the phenomenological models are we have discussed that there are black box types and they provide no information how the separation is actually occurring.

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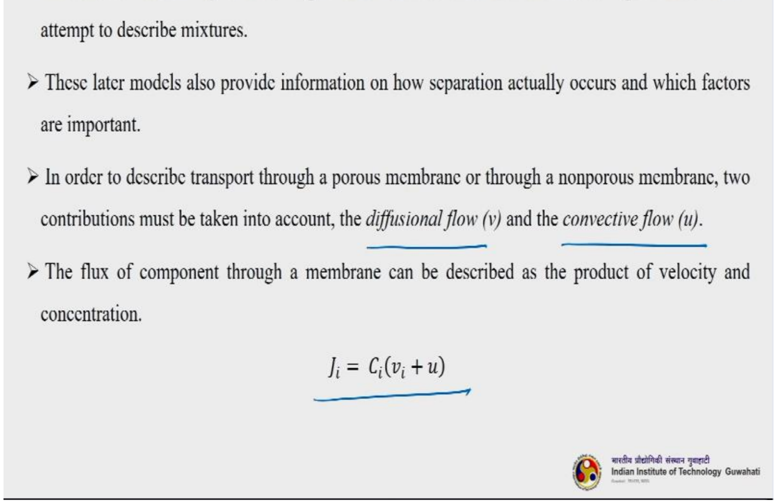

- Mechanistic models try to relate separation with structural-related membrane parameters in an attempt to describe mixtures.
- These later models also provide information on how separation actually occurs and which factors are important.
- In order to describe transport through a porous membrane or through a nonporous membrane, two contributions must be taken into account, the *diffusional flow (v)* and the *convective flow (u)*.
- The flux of component through a membrane can be described as the product of velocity and concentration.

$$\underline{J_i = C_i(v_i + u)}$$

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So, that is why you have discussed many times different models whether it is Hagen Poiseuille equation Kozeny Carman equation are expressing the flux in terms of frictional process also and even in expressing them in terms of here osmotic pressure difference also holds the key to understand what is the transport and how the transport is actually happening. A mechanistic models try to relate separation with structural related membrane parameters in an attempt to describe mixtures.

Now, these later models also provide information on how separation actually occurs, and which factors are important now in order to describe transport through a porous membrane or through a non porous membrane, 2 contributions must be taken into account. So that the diffusional flow and that convective flow now you can write that why so, flux J i = C i in to v i + u, So product of the velocity and the concentration.

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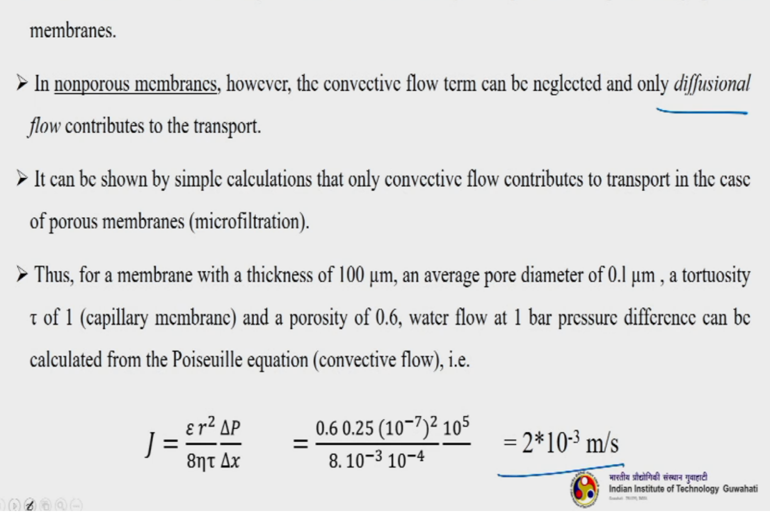

- The contribution of *convective flow* is the main term in any description of transport through porous membranes.
- In nonporous membranes, however, the convective flow term can be neglected and only *diffusional flow* contributes to the transport.
- It can be shown by simple calculations that only convective flow contributes to transport in the case of porous membranes (microfiltration).
- Thus, for a membrane with a thickness of 100 µm, an average pore diameter of 0.1 µm , a tortuosity τ of 1 (capillary membrane) and a porosity of 0.6, water flow at 1 bar pressure difference can be calculated from the Poiseuille equation (convective flow), i.e.

$$J = \frac{\varepsilon r^2}{8\eta\tau}\frac{\Delta P}{\Delta x} \qquad = \frac{0.6\ 0.25\ (10^{-7})^2}{8.\ 10^{-3}\ 10^{-4}}\frac{10^5}{} \quad = 2*10^{-3}\ \text{m/s}$$

The concentration of convective flow is the main term in any description of transport through porous membrane. In nonporous membranes however, the convective flow term can be neglected and only diffusional flow that is contributes to the transport. It can be shown by simple calculations that only convective flow contributes to transport in case of porous membranes, especially in case of micro filtration where the pore sizes are bigger thus for a membrane with the thickness of this is an example, Let us considered a membrane which is a thickness of 100 micron and average pore diameter point 1 micron at tortuosity tau of 1 assuming capillary membrane and the porosity of point 6 water flow at 1 bar pressure difference can be calculated from the poiseuille equation. So, it is convective flowing we find 10 into 10 power of - 3 meter per second.

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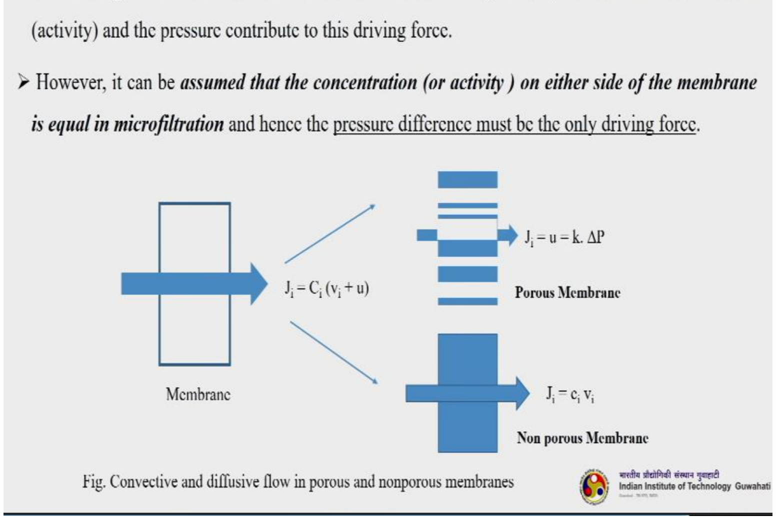

- The driving force for diffusion is the difference in chemical potential, and both the concentration (activity) and the pressure contribute to this driving force.
- However, it can be ***assumed that the concentration (or activity) on either side of the membrane is equal in microfiltration*** and hence the pressure difference must be the only driving force.

Membrane

$J_i = C_i (v_i + u)$

$J_i = u = k. \Delta P$

Porous Membrane

$J_i = c_i\, v_i$

Non porous Membrane

Fig. Convective and diffusive flow in porous and nonporous membranes

Now, the driving force for diffusion is the difference in chemical potential and both the concentration or activity and the pressure contribute to this driving force. However, it can be assume that the concentration or the activity on either side of the membrane is equal in micro filtration and hence the pressure differences must be the only driving force you can see this particularly scheme where membrane as transport is shown into different types of membrane one is porous membrane and non porous membrane. So, both converting and diffusing flow is happening.

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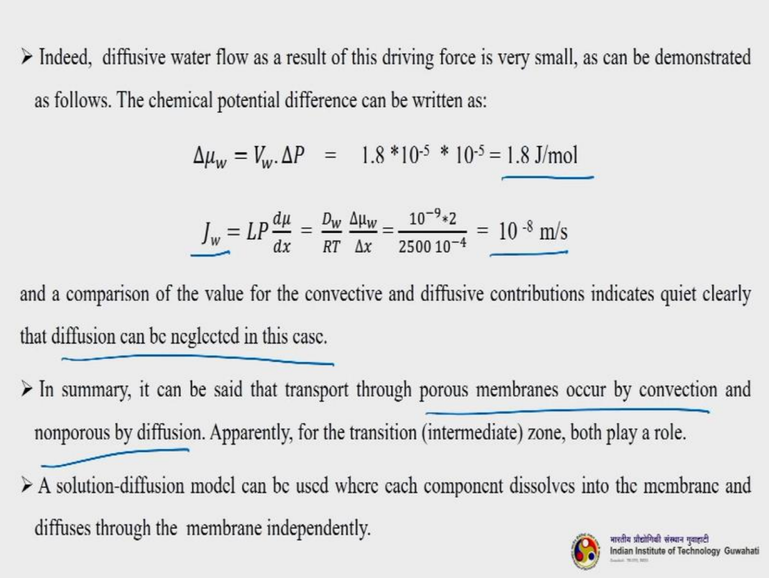

- Indeed, diffusive water flow as a result of this driving force is very small, as can be demonstrated as follows. The chemical potential difference can be written as:

$$\Delta\mu_w = V_w . \Delta P \quad = \quad 1.8 * 10^{-5} * 10^{-5} = \underline{1.8 \text{ J/mol}}$$

$$\underline{J_w} = LP\frac{d\mu}{dx} = \frac{D_w}{RT}\frac{\Delta\mu_w}{\Delta x} = \frac{10^{-9} * 2}{2500\ 10^{-4}} = \underline{10^{-8} \text{ m/s}}$$

and a comparison of the value for the convective and diffusive contributions indicates quiet clearly that diffusion can be neglected in this case.

- In summary, it can be said that transport through porous membranes occur by convection and nonporous by diffusion. Apparently, for the transition (intermediate) zone, both play a role.
- A solution-diffusion model can be used where each component dissolves into the membrane and diffuses through the membrane independently.

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Indeed, the diffusive water flow as a result of this driving force is very small and can be demonstrated as follows. So, you can calculate delta mu w = 1.8 Jules per mole and flux or water flux = 10 power of - 8 meter per second, so, if you compare these values for convective and diffusive contributions that it indicates that diffusion can be neglected in this cases, because it is very less the value is very small.

So, it can be neglected in summary it can be said that transport through porous membrane occur by convection and non porous by diffusion. So, porous membrane usually convection happening and non porous diffusion happening, apparently for the transition which we discussed just few times before or we also call a intermediate zone, in which both convection and diffusion play a role. So, solution diffusion model can be used where each component deserves into the membrane and diffuse through the membrane independently.

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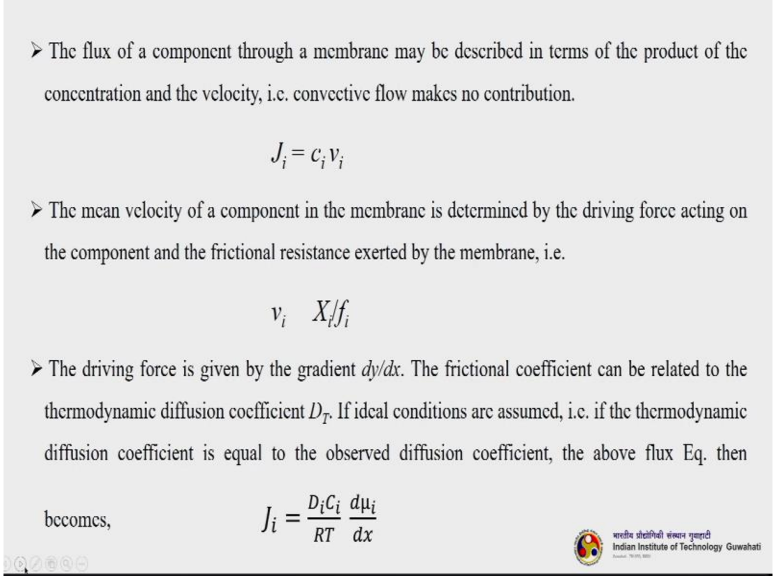

- The flux of a component through a membrane may be described in terms of the product of the concentration and the velocity, i.e. convective flow makes no contribution.

$$J_i = c_i v_i$$

- The mean velocity of a component in the membrane is determined by the driving force acting on the component and the frictional resistance exerted by the membrane, i.e.

$$v_i \quad X_i/f_i$$

- The driving force is given by the gradient *dy/dx*. The frictional coefficient can be related to the thermodynamic diffusion coefficient D_T. If ideal conditions are assumed, i.e. if the thermodynamic diffusion coefficient is equal to the observed diffusion coefficient, the above flux Eq. then becomes,

$$J_i = \frac{D_i c_i}{RT}\frac{d\mu_i}{dx}$$

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So, the flux of a component through a membrane may be described in terms of the product of the concentration and the velocity. So, j = c i v i so, that is convective flow, no contribution. So, the mean velocity can be calculated from this equation v i = X i / f i, the driving force is given by the gradient dy / dx. The frictional corporation can be related to the thermodynamic diffusion coefficient, if ideal conditions are assumed and if the thermodynamic diffusion coefficient D t is equal to the observed diffusion coefficient, that above equation can then be becomes J i = D i c i / RT into d mu i / dx.

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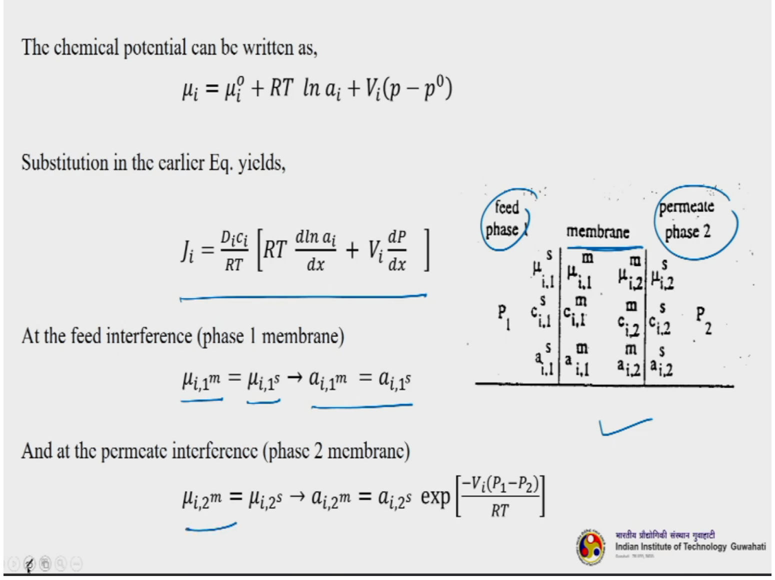

The chemical potential can be written as,

$$\mu_i = \mu_i^o + RT\ \ln a_i + V_i(p - p^0)$$

Substitution in the earlier Eq. yields,

$$\underline{J_i = \frac{D_i c_i}{RT}\left[RT\frac{d\ln a_i}{dx} + V_i\frac{dP}{dx}\ \right]}$$

At the feed interference (phase 1 membrane)

$$\underline{\mu_{i,1^m}} = \underline{\mu_{i,1^s}} \rightarrow \underline{a_{i,1^m} = a_{i,1^s}}$$

And at the permeate interference (phase 2 membrane)

$$\underline{\mu_{i,2^m}} = \mu_{i,2^s} \rightarrow a_{i,2^m} = a_{i,2^s}\ \exp\left[\frac{-V_i(P_1 - P_2)}{RT}\right]$$

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So, you have seen this particular equation our last class, that we expressed the chemical potential in this particular form and if you substitute this in earlier equation, we get J i in something like this, at the feed interphase. This you can see how the notations are given actually, this is feed phase. This is permeate phase and this is the membrane phase. So, the membranes have denoted by m, whereas in feed side as well as permeate side it is denoted by s.

So, at the feed interface we can write chemical potential of species 1 in inside the membrane h is equal to that of the solute side or feed side or permeate side any one. So, hence activity also can be written in the same manner and then the permeate interference also it can write something like this.

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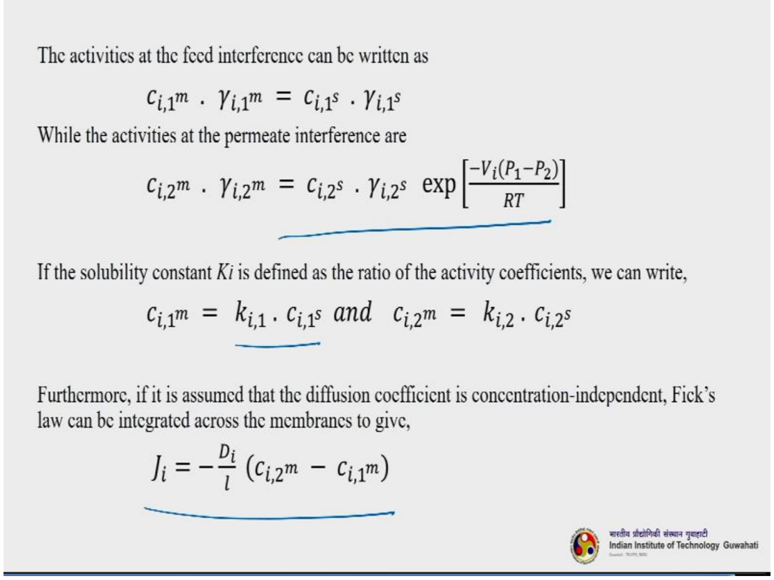

The activities at the feed interference can be written as

$$c_{i,1^m} \cdot \gamma_{i,1^m} = c_{i,1^s} \cdot \gamma_{i,1^s}$$

While the activities at the permeate interference are

$$c_{i,2^m} \cdot \gamma_{i,2^m} = \underline{c_{i,2^s} \cdot \gamma_{i,2^s} \ \exp\left[\frac{-V_i(P_1-P_2)}{RT}\right]}$$

If the solubility constant *Ki* is defined as the ratio of the activity coefficients, we can write,

$$c_{i,1^m} = \underline{k_{i,1} \cdot c_{i,1^s}} \ and \ \ c_{i,2^m} = k_{i,2} \cdot c_{i,2^s}$$

Furthermore, if it is assumed that the diffusion coefficient is concentration-independent, Fick's law can be integrated across the membranes to give,

$$\underline{J_i = -\frac{D_i}{l}\left(c_{i,2^m} - c_{i,1^m}\right)}$$

The activities at the feed interference can be written in terms of c i 1 s into gamma i 1 s and similarly we can write the activities of the permeate interference some is this and if the solubility constant k i is defined as the ratio of the activity coefficients, we can write c i 1 m that is the constants inside the membrane equals to k i 1 into Ci1s concentration of the permeate side and furthermore it is assumed that the diffusion coefficients is concentration dependent independent, Fick's law can be integrated. So, you can write the flux J i = - D i / l c i 2 m - c i 1 m.

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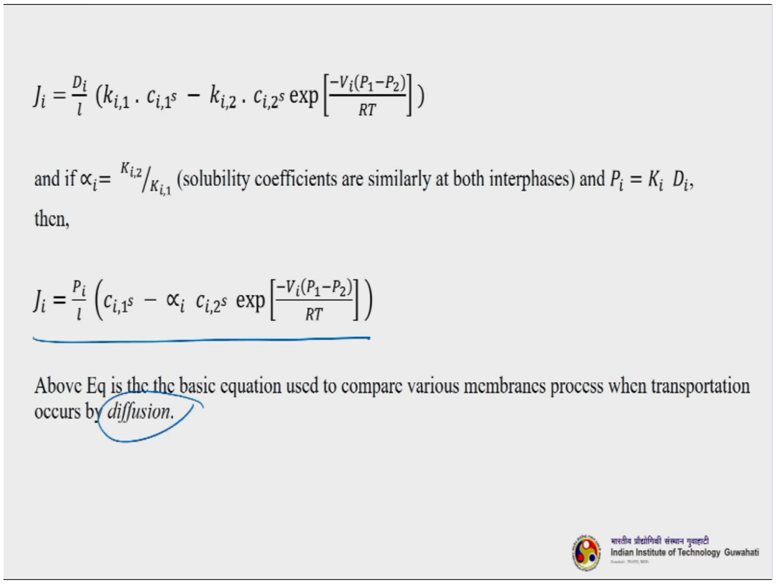

$$J_i = \frac{D_i}{l}\left(k_{i,1} \cdot c_{i,1^s} - k_{i,2} \cdot c_{i,2^s} \exp\left[\frac{-V_i(P_1 - P_2)}{RT}\right]\right)$$

and if $\propto_i = {}^{K_{i,2}}/_{K_{i,1}}$ (solubility coefficients are similarly at both interphases) and $P_i = K_i\ D_i$,

then,

$$\underline{J_i = \frac{P_i}{l}\left(c_{i,1^s} - \propto_i\ c_{i,2^s}\ \exp\left[\frac{-V_i(P_1 - P_2)}{RT}\right]\right)}$$

Above Eq is the the basic equation used to compare various membranes process when transportation occurs by *diffusion.*

So, J i can be expressed in terms of the equation after in substituting from the earlier equations, and if you write alpha = k i2 / k i1 that is the solubility coefficients similar at both interphases and P i = K i D i, then we can express the flux in this particular manner in terms of alpha and the pressure differences, that is the pressure at upstream side and the downstream P 1 and P 2. So above equation is the basic equation used to compare various membrane processes when the transportation occurs by diffusion.

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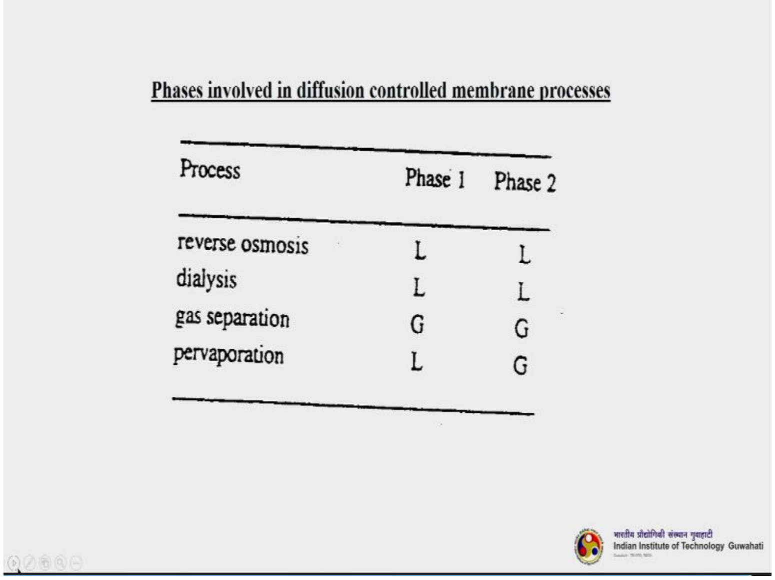

Phases involved in diffusion controlled membrane processes

Process	Phase 1	Phase 2
reverse osmosis	L	L
dialysis	L	L
gas separation	G	G
pervaporation	L	G

So, this is the phases involved in diffusion control membrane processes. There you can see that there can be 2 different types of phases can be possible in reverse osmosis. It is liquid liquid in dialysis it is liquid liquid in gas separation it is gas and gas in pervaporation it is liquid and gas.

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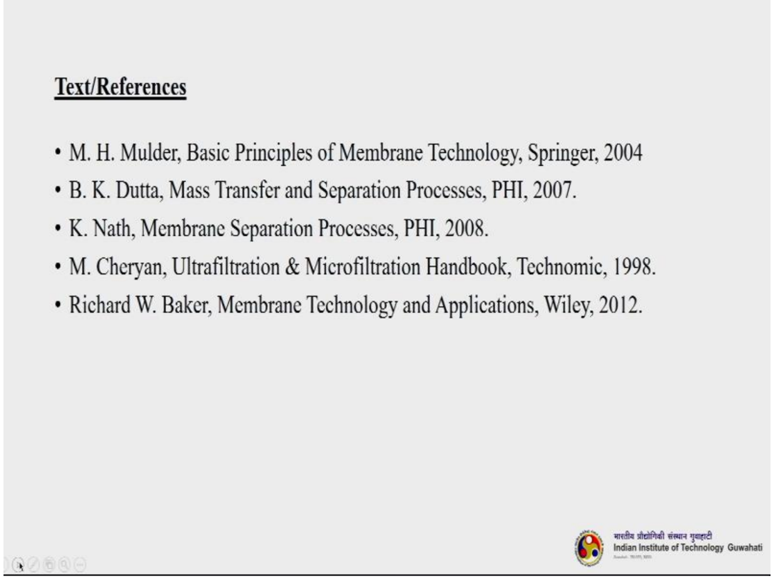

Text/References

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So, today's lecture is also mostly taken from the textbook Mulder you can also refer Becker and other books to restrict.

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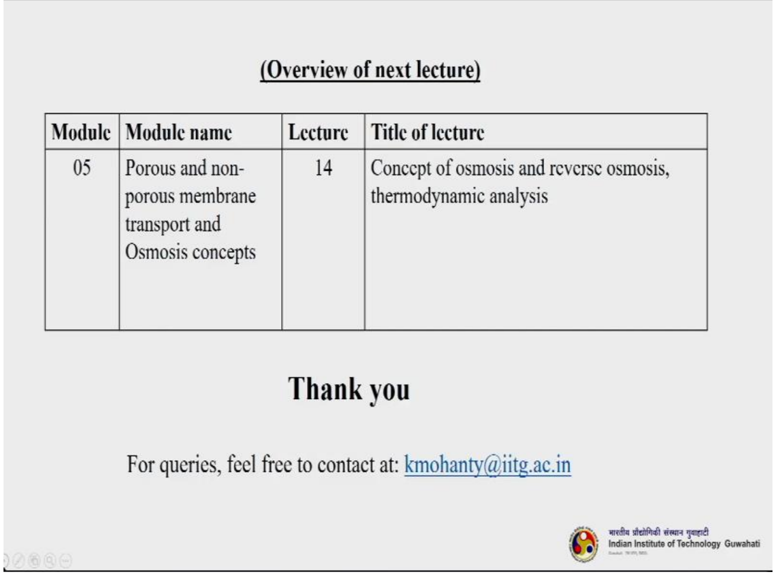

(Overview of next lecture)

Module	Module name	Lecture	Title of lecture
05	Porous and non-porous membrane transport and Osmosis concepts	14	Concept of osmosis and reverse osmosis, thermodynamic analysis

Thank you

For queries, feel free to contact at: kmohanty@iitg.ac.in

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So, the next lecture under this particular module will discuss the concept of osmosis, reverse osmosis take into account the thermodynamic analysis. So, thank you very much and if you have any questions or queries do feel free to write to me it came on at kmohanty@iitg.ac.in.Thank you.