Membrane Technology
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Lecture – 12
Passive transport, Active transport, Description of transport process

Good morning students, today is lecture 12 under module 4. In this lecture, today we will discuss about the membrane transport. So, what is passive transport? What is active transport, then we will see what are the phenomenological equations, not the different types of driving forces. And then we will discuss the Onsager's non equilibrium thermodynamics.

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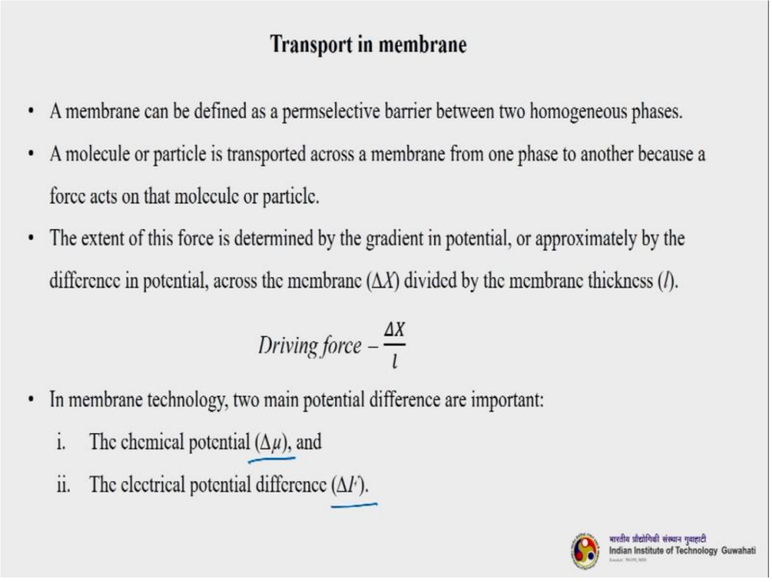

Transport in membrane

- A membrane can be defined as a permselective barrier between two homogeneous phases.
- A molecule or particle is transported across a membrane from one phase to another because a force acts on that molecule or particle.
- The extent of this force is determined by the gradient in potential, or approximately by the difference in potential, across the membrane (ΔX) divided by the membrane thickness (l).

$$\text{Driving force} - \frac{\Delta X}{l}$$

- In membrane technology, two main potential difference are important:
  i. The chemical potential ($\Delta\mu$), and
  ii. The electrical potential difference (ΔV).

So, a membrane can be defined as a permselective barrier between 2 homogeneous versus a molecule or particle is transported across the membrane from one phase to another phase, because force acts on that molecule or particle. We just revisit what we have discussed in our earlier classes. The extent of this force is determined by the gradient in potential or approximately by difference in potential across the membrane divided by the membrane thickness.

So, if you remember many times I have told you in our subsequent discussions, then the resistance to the transport is one of the most important thing that has to be taken care of. So, in your revising of making a membrane or when you are devising developing a membrane process itself. So, one of the most important parameter is the thickness of the membrane. So, it is quite understood that for a porous membrane or even perceived and non-porous membrane also.

The thickness also plays an important role more the thickness the more will be the resistance to the flow. So, the driving force is given by the difference in potential by the thickness of membrane. So, usually we come across 2 different types of potential difference, one is the chemical potential difference delta mu which we have discussed in our earlier classes. And then there is the electrical potential difference that delta f.

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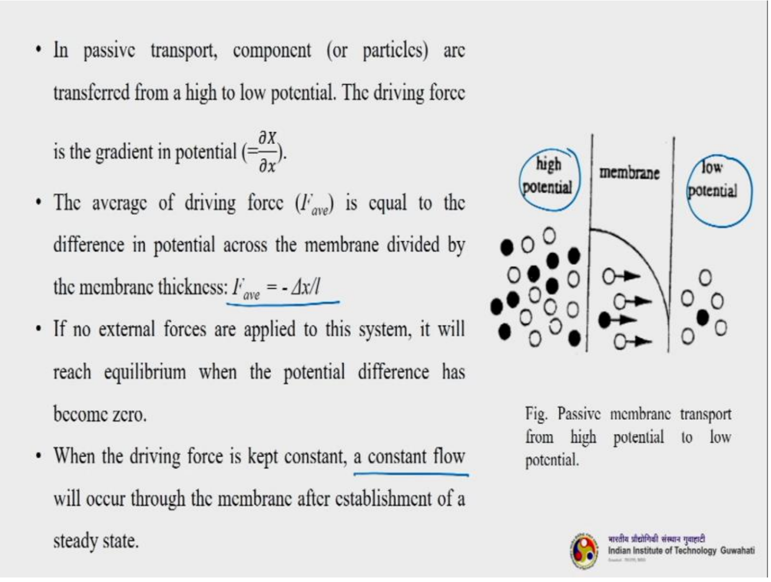

- In passive transport, component (or particles) are transferred from a high to low potential. The driving force is the gradient in potential ($=\frac{\partial X}{\partial x}$).
- The average of driving force (F_{ave}) is equal to the difference in potential across the membrane divided by the membrane thickness: $F_{ave} = -\Delta X/l$
- If no external forces are applied to this system, it will reach equilibrium when the potential difference has become zero.
- When the driving force is kept constant, a constant flow will occur through the membrane after establishment of a steady state.

Fig. Passive membrane transport from high potential to low potential.

Now, in passive transport component or particles of transferred from high to low potential, so, we have a high potential and then there is a low potential and in between there is a membrane. So, the transport of solutes or particles are happening due to the gradient in potential from high to low and the gradient is delta X / delta x. x is the basically a distance and the average driving force is equal to the difference in potential across the membrane divided by the membrane thickness.

So, this is a average driving force and if no external forces is applied to the system it will reach equilibrium when the potential difference has become 0. So, if we are not applying any particular forces on to this type of system, passive transport, then the system will reach equilibrium when the potential difference almost become 0. So, when the driving force is kept constant a constant flow will occur through the membrane after establishment of a steady state. And this is the schematic source how actually the passive transport is happening from high potential to low potential.

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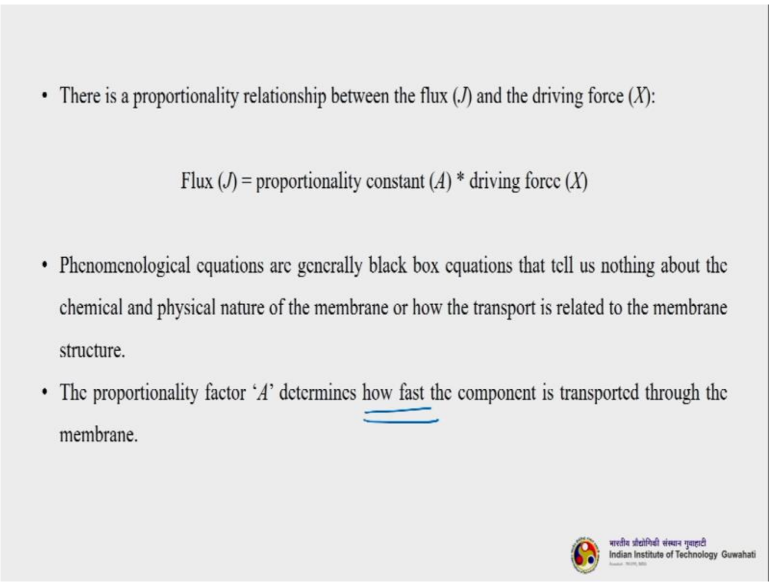

- There is a proportionality relationship between the flux (J) and the driving force (X):

Flux (J) = proportionality constant (A) * driving force (X)

- Phenomenological equations are generally black box equations that tell us nothing about the chemical and physical nature of the membrane or how the transport is related to the membrane structure.
- The proportionality factor 'A' determines how fast the component is transported through the membrane.

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So, the proportionality relationship between the flux and the driving force is given by this particular ecosystem. A flux equals to proportionality constant which is usually denoted by A into driving force. Now phenomenological equations are generally they are black box type of equations, which tells us nothing about the chemical and physical nature of the membrane. Please note that the membrane itself also plays a very important role.

That means, the membrane itself means that type of polymer or type of material that is being used to prepare membrane and what is their physical chemical properties, and then how the transport is related to the membrane structure that is also this phenomenological equations silent about, it is not telling because, you see, the equation is just proportionality constant into the driving force.

So, what is the proportionality constant proportionality constant determines how fast the component is transported through the membrane. It has nothing to do it the membrane material and how the transport is happening. It is just telling them how fast the component is transported through the membrane.

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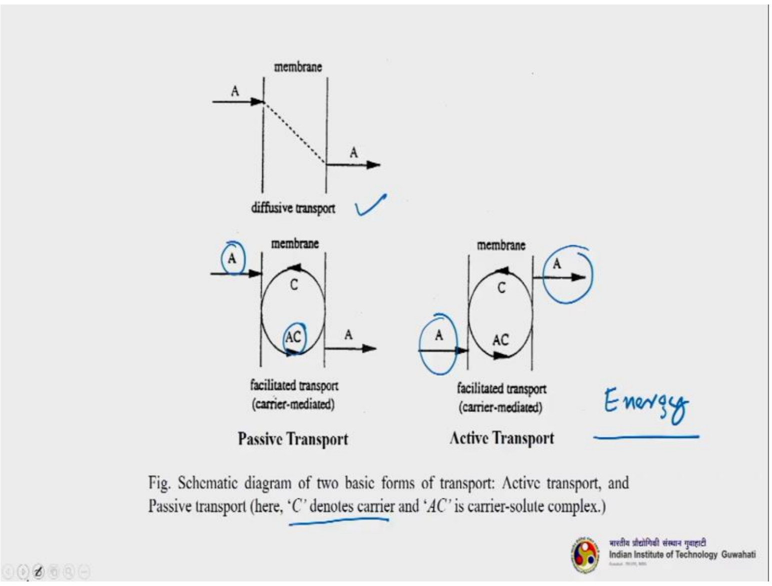

Fig. Schematic diagram of two basic forms of transport: Active transport, and Passive transport (here, '*C*' denotes carrier and '*AC*' is carrier-solute complex.)

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So, have a close look at this schematic diagrams were showing 2 basic forms of transport active and passive transport. So, this is what you can see this. We just discussed in the earlier slide this one. High potential to lower potential now please understood that this type of transport which is passive transport and also be carried out with the help of this molecule usually called carrier. So denoted by C.

Now what is happening? Why do we need this? These are called facilitated transport. We will discuss this in one of our classes later on, but let us try to understand the concept. What is this? What is the meaning of facilitated transport and when do we need it? It may happen that sometimes there are certain components or molecules which are not able to transport through the membrane by virtue of the concentration gradient or the potential gradient itself. But we need to transport it on into separate it. So, what should we do that?

So, in that situations we can employ a molecule which is called a carrier molecule, which are usually imparted inside the membranes. They are available freely or suspended freely inside the membrane parts or there may be fixed also it depends. So, this carrier molecule will bind the solute which is A here and for me intermediate complex called AC which is highly unstable and then it will go to the permeate side.

So, basically A is binding to the C AC is forming, that is the unstable carrier solute complex. When it reaches to the permeate side, the A is defuses back defuses to the permeate side. So this is called carrier mediator transport facilitated transport. Now if I want to have this type of transport, when I am moving from a low potential here, you see that this is a low potential and this is too high potential, then this is called active transport.

So that means I am going against the gradient of the potential difference. So to do that, these are mostly biological transport are like this. Biological system transport something like this. So, to depth we need something which is called energy. So, we need an extra energy to achieve this transport because try to understand that we are moving from a lower concentration to higher concentration not low potential to high potential to achieve that. I need something some extra energy, that energy will be supplied by forms of chemical energy or in case of this chemical systems or ATPs in case of biological systems.

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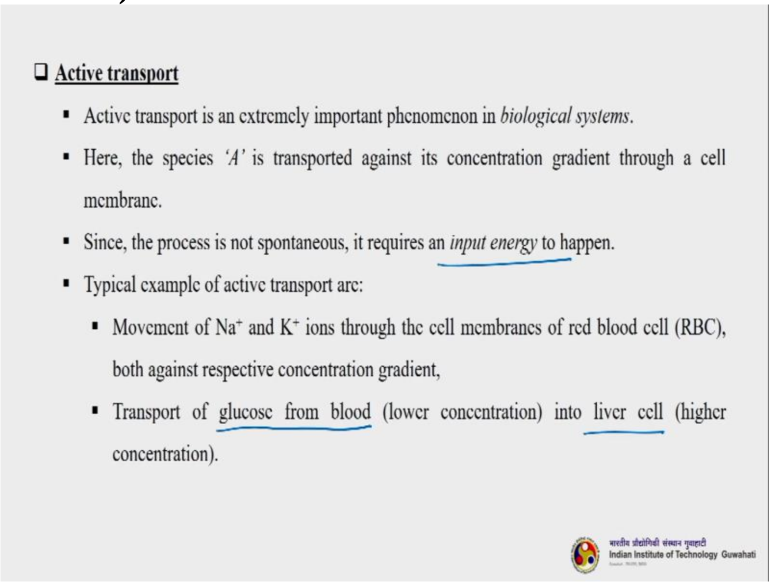

❑ **Active transport**

- Active transport is an extremely important phenomenon in *biological systems*.
- Here, the species *'A'* is transported against its concentration gradient through a cell membrane.
- Since, the process is not spontaneous, it requires an *input energy* to happen.
- Typical example of active transport are:
  - Movement of Na^+ and K^+ ions through the cell membranes of red blood cell (RBC), both against respective concentration gradient,
  - Transport of glucose from blood (lower concentration) into liver cell (higher concentration).

So, active transport is an extremely important phenomenon is biological systems. Here the species A is transported against its concentration gradient through a cell membrane. We are talking about the biological systems here in this case, say for example, since the process is not spontaneous, it requires an input energy to happen. This is what I just told you, so, there are 2 classic examples.

So, one is the movement of sodium and potassium ions. So, that is membrane of the red blood cell the RBC both against the concentration gradient. Then transport of glucose from blood to liver cell. So, actually the glucose concentration in the liver cell is much higher than that of the blood cell. So, but the liver cells needs the glucose a substrate to survive. So, for that they need to have intake or more intakes of glucose from the blood cell.

So, the in the blood cell the glucose is in lower concentration that of the sloka cell in that of the liver cell. So, basically what is happening, the glucose is moving from a lower potential to a higher potential. So, this is how this happens. I will just try to show you in the next slide.

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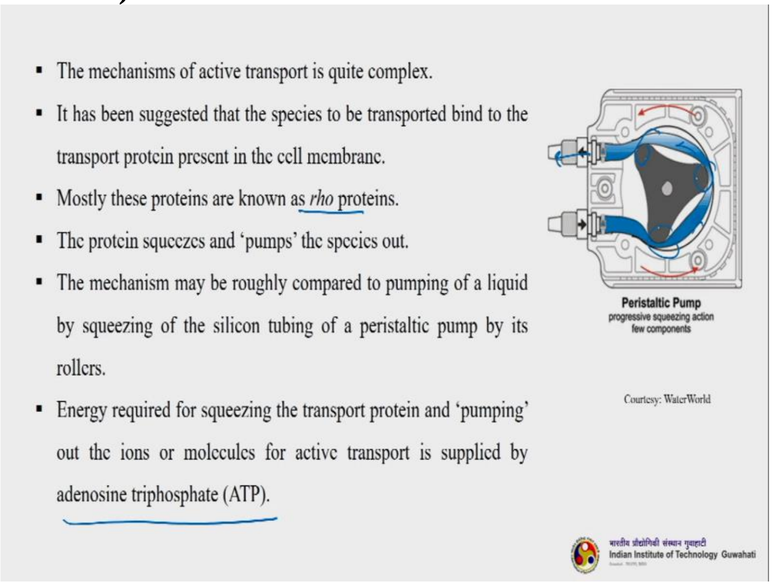

- The mechanisms of active transport is quite complex.
- It has been suggested that the species to be transported bind to the transport protein present in the cell membrane.
- Mostly these proteins are known as *rho* proteins.
- The protein squeezes and 'pumps' the species out.
- The mechanism may be roughly compared to pumping of a liquid by squeezing of the silicon tubing of a peristaltic pump by its rollers.
- Energy required for squeezing the transport protein and 'pumping' out the ions or molecules for active transport is supplied by adenosine triphosphate (ATP).

Peristaltic Pump
progressive squeezing action
few components

Courtesy: WaterWorld

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So, the mechanism of active transport is quite complex. It has been suggested that species to be transported bind to the transport protein present in the cell membrane. So, there are certain proteins present in the cell membranes of even ourselves also, and animals and all mammals. So those proteins are called transport protein some of the specific proteins are also called rho proteins.

Now, what is the job of these proteins? These proteins will bind this sodium, potassium or glucose and then by binding it. Then when it binds it, it will help in to transport this particular sodium, potassium or glucose across the cell membrane there is a cell membrane. So, that sodium, potassium or glucose needs to cross the cell membrane. So, these proteins will help them to cross them. So, once they reach the other side of the cell membrane, permeate side.

Let us say, it will diffuse out whether it is sodium, potassium or glucose there are many other things also, it is not only limited to these 3, so, the protein actually squeezes and then pumps out the pumps the species which is already something like a peristaltic mechanism. You see, this is a peristaltic pump and a mechanism I am just trying to show you to understand how the cell membrane actually works. So, you see here, this is the input.

These are silicon tubes which is getting squeezed here, squeezing then it is living against squeezing than it is living against squeezing than it is coming out. So, this is the way the peristaltic pump actually works actually our digestive system in humans or mammals, it also mostly works in this type of mechanism. So, it squeezes in squeezes out squeezes in squeezes out. And energy required for squeezing the transport protein and pumping out the ions or molecules for active transport is supplied by adenosine triphosphate in case of the biological systems.

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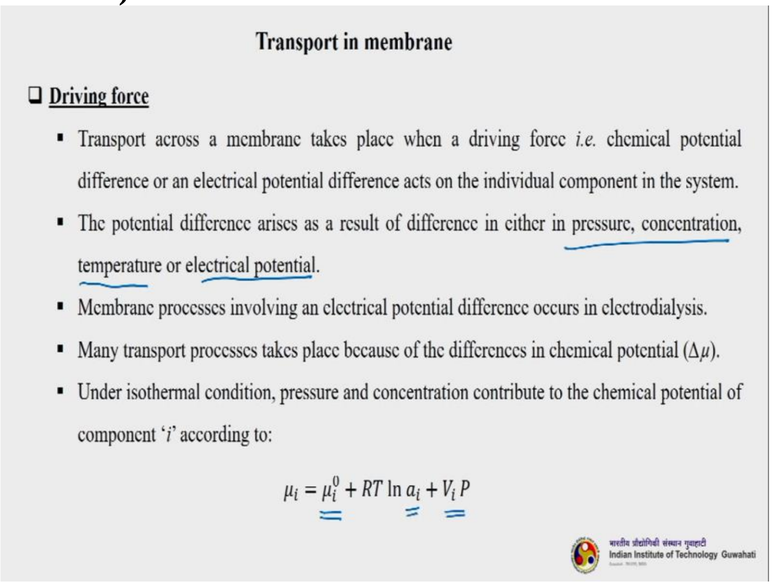

Transport in membrane

❑ **Driving force**

- Transport across a membrane takes place when a driving force *i.e.* chemical potential difference or an electrical potential difference acts on the individual component in the system.
- The potential difference arises as a result of difference in either in pressure, concentration, temperature or electrical potential.
- Membrane processes involving an electrical potential difference occurs in electrodialysis.
- Many transport processes takes place because of the differences in chemical potential ($\Delta\mu$).
- Under isothermal condition, pressure and concentration contribute to the chemical potential of component '*i*' according to:

$$\mu_i = \mu_i^0 + RT \ln a_i + V_i P$$

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So, now, let us understand the driving forces. So, transport across a membrane takes place when a driving force that is chemical potential difference or electrical potential difference acts on the individual component in this system. The potential difference arises as a result of differences in either in pressure, concentration, temperature or electrical potential. Since, I told you earlier also since I cannot measure chemical potential directly.

So we always express chemical potential in terms of certain measurable parameters may it be pressure may it be concentration it may be temperature. So, membrane processes involving an electrical potential difference usually occurs in cases of electrodialysis. So the electrodialysis and many transport processes takes place because of the differences in chemical potential under isothermal conditions pressure concentration contribute to the chemical potential of the component i.

So, let us see these equations. Mu i is the chemical potential of the species i = mu i 0. This is a constant for the pure species. So, basically this is chemical potential of the same species but pure. Then RT ln a i, a i is the activity then V i P. So, V is the molar volume and P is the pressure.

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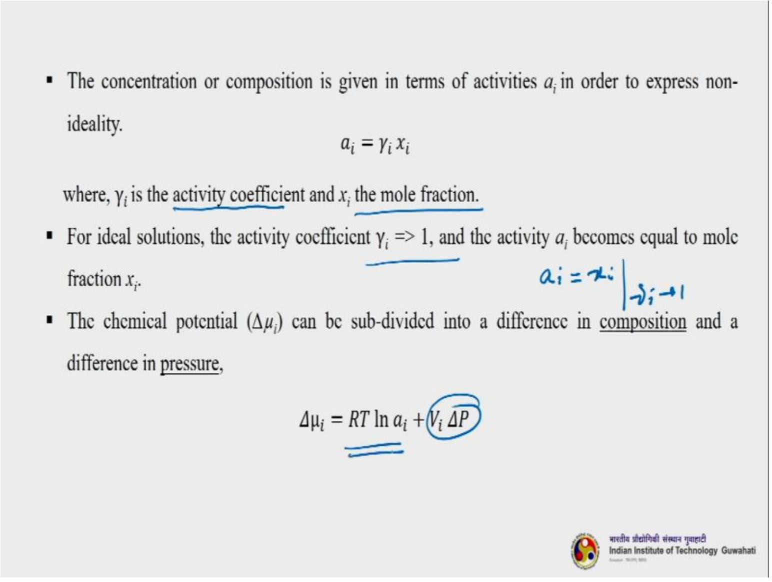

- The concentration or composition is given in terms of activities a_i in order to express non-ideality.

$$a_i = \gamma_i x_i$$

where, γ_i is the activity coefficient and x_i the mole fraction.

- For ideal solutions, the activity coefficient γ_i => 1, and the activity a_i becomes equal to mole fraction x_i.

$$a_i = x_i \Big|_{\gamma_i \to 1}$$

- The chemical potential ($\Delta\mu_i$) can be sub-divided into a difference in composition and a difference in pressure,

$$\Delta\mu_i = \underline{\underline{RT}} \ln a_i + \boxed{V_i \Delta P}$$

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So, the concentration or composition is given in terms of activity in order to express the non-ideality. So, activity can be given by this is gamma x i. where gamma i activity coefficient and x i is the mole fraction. Now, we know most of our ideal cases your activity coefficients usually tends to 1. So then it becomes equal to the mole fraction. So a i becomes x i when gamma i becomes 1.

So, the chemical potential can be subdivided into a difference in composition and difference in pressure. Now, you can understand that how the difference in chemical potential is basically due to 2 terms. So, this is your pressure term and this is your composition or concentration terms.

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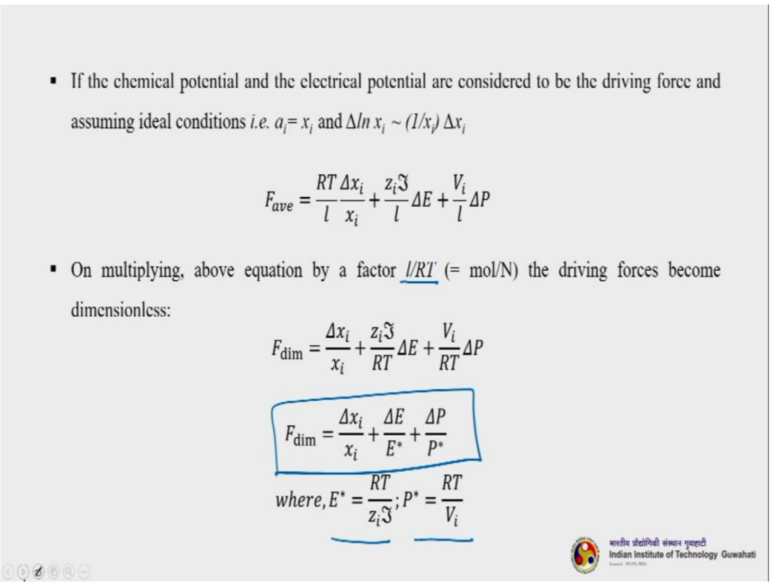

- If the chemical potential and the electrical potential are considered to be the driving force and assuming ideal conditions *i.e.* $a_i = x_i$ and $\Delta ln\, x_i \sim (1/x_i)\, \Delta x_i$

$$F_{ave} = \frac{RT}{l}\frac{\Delta x_i}{x_i} + \frac{z_i \Im}{l}\Delta E + \frac{V_i}{l}\Delta P$$

- On multiplying, above equation by a factor $\underline{l/RT}$ (= mol/N) the driving forces become dimensionless:

$$F_{\dim} = \frac{\Delta x_i}{x_i} + \frac{z_i \Im}{RT}\Delta E + \frac{V_i}{RT}\Delta P$$

$$\boxed{F_{\dim} = \frac{\Delta x_i}{x_i} + \frac{\Delta E}{E^*} + \frac{\Delta P}{P^*}}$$

$$where, E^* = \underline{\frac{RT}{z_i \Im}}; P^* = \underline{\frac{RT}{V_i}}$$

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So, if the chemical potential and the electrical potential are considered to be the driving force and assuming ideal conditions that means a i activity equals to mole fraction and del of a ln x i = 1 over x i del x i. We can express the average driving force like this, this equals to RT / l delta x i / x i, then z i / l delta E V i / l delta P. So, l is the thickness of the membrane. So now you have to just rearranging the thing.

So on multiplying the above equation by a factor l / RT. So, we just want to make these groups as dimensionless groups. So, we will get force dimensionless is delta x i / x i then this particular group delta E V i, / RT delta P. So, again we can write in terms of constants. So, this is the equation actually. Delta x i / x i + delta E / E star + delta P by P star. So E star is this, this is constant and P star is RT / V i.

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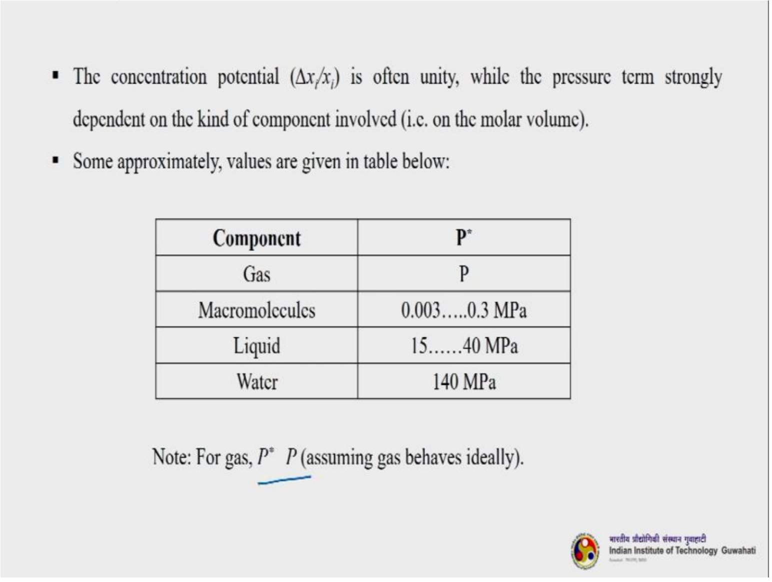

- The concentration potential ($\Delta x_i/x_i$) is often unity, while the pressure term strongly dependent on the kind of component involved (i.e. on the molar volume).
- Some approximately, values are given in table below:

Component	P^*
Gas	P
Macromolecules	0.003…..0.3 MPa
Liquid	15……40 MPa
Water	140 MPa

Note: For gas, $\underline{P^* \;\; P}$ (assuming gas behaves ideally).

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So, the concentration potential is often unity by the pressure term strongly dependent on the kind of component involved that is on the molar volume some approximately values are given below. Actually if it is gas than it is P if it is macromolecules it is 0.003 to 0.3 mega Pascal like this. For gases P star equals to P. We assume that gases we have ideally.

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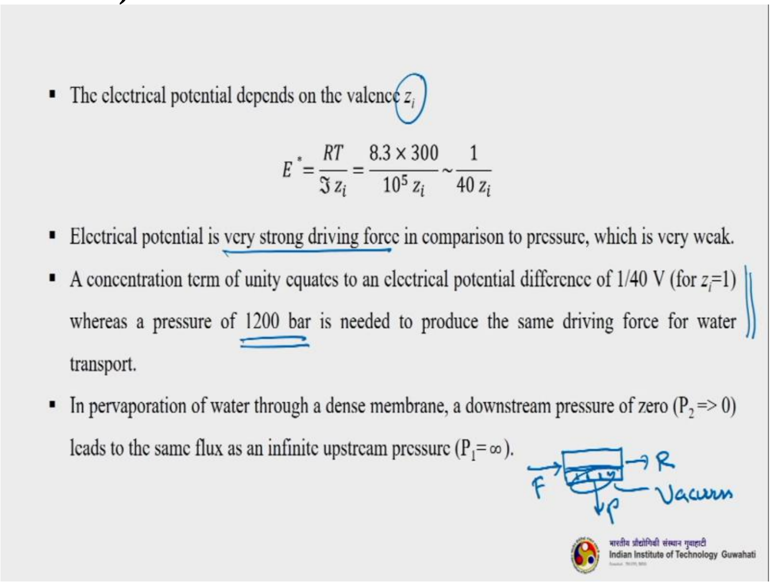

- The electrical potential depends on the valence z_i

$$E^* = \frac{RT}{\Im z_i} = \frac{8.3 \times 300}{10^5 z_i} \sim \frac{1}{40 z_i}$$

- Electrical potential is very strong driving force in comparison to pressure, which is very weak.
- A concentration term of unity equates to an electrical potential difference of 1/40 V (for z_i=1) whereas a pressure of 1200 bar is needed to produce the same driving force for water transport.
- In pervaporation of water through a dense membrane, a downstream pressure of zero (P_2 => 0) leads to the same flux as an infinite upstream pressure ($P_1 = \infty$).

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The electrical potential depends on the valence z i. So, z i is equal to this is valency of the species i. So, this is 8.3 into 300 divided by 10 power of 5 z i. So 1 over 40 z i. So, electrical potential is very strong driving force it is a very strong driving force in comparison to pressure which is weak force, a concentration term of unity equates to an electrical potential difference of 1 / 40 V for z i = 1 whereas a pressure of 1200 bar is needed to produce the same driving force for water transport.

So, what we understand from, this is that if we want to have the same type of driving force, let us prefer water transport having any electrical potential difference as well as a pressure difference. So for an electrical potential difference 1 \ 40 V is enough to do that to get that driving force however, the same driving force if I want to achieve through the pressure then I have to use 1200 bar which is huge pressure you can understand that.

So in pervaporation of water through a dense membrane a downstream pressure of 0 leads to the same flux as an infinite upstream pressure. So, we will discuss pervaporation in detail in some classes in our subsequent classes. So pervaporation is a system in which actually I am just in a nutshell I am telling so this is a membrane. So what is happening. The feed is coming here. So the permeate is coming and this will get returned.

So what is happening in pervaporation the permeate vaporization? So whatever permeate is coming here, that is getting vacuumed. So, why do we do that so, we create a low vapor pressure so that they will condense. This is the actually mechanism. So, this is pervaporation membranes are also mostly these are non-porous membranes. So, the mechanism is solution deficient.

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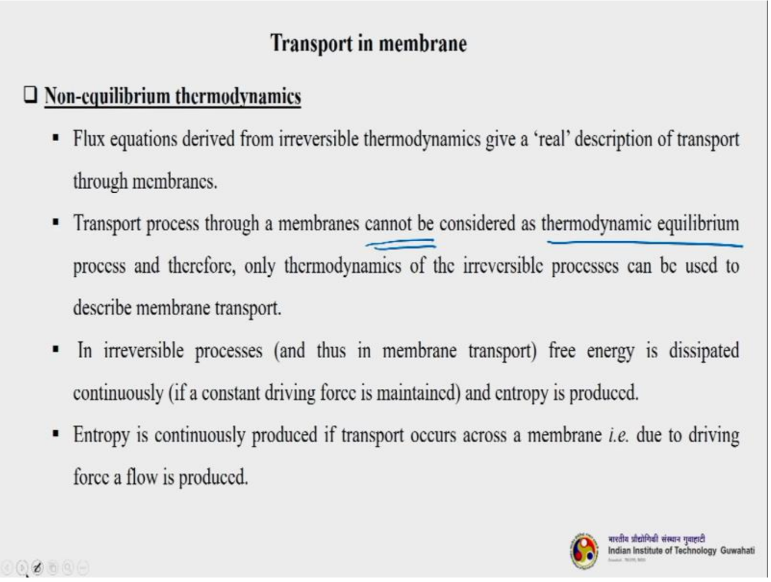

Transport in membrane

❑ **Non-equilibrium thermodynamics**

- Flux equations derived from irreversible thermodynamics give a 'real' description of transport through membranes.
- Transport process through a membranes cannot be considered as thermodynamic equilibrium process and therefore, only thermodynamics of the irreversible processes can be used to describe membrane transport.
- In irreversible processes (and thus in membrane transport) free energy is dissipated continuously (if a constant driving force is maintained) and entropy is produced.
- Entropy is continuously produced if transport occurs across a membrane *i.e.* due to driving force a flow is produced.

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Now, let us discuss non equilibrium thermodynamics. Now flux equations derived from irreversible thermodynamics give a real description of transport through membranes. However transport process through membrane cannot be considered as thermodynamically equilibrium process. This we have discussed in our first or second class. If you remember and therefore only thermodynamics of the irreversible processes can be used to describe membrane transport.

In irreversible processes and thus in membrane transport, free energy is dissipated continuously that in case the constant driving forces maintained and then entropy is produced. Now entropy is continuously produced if transport across membrane that is due to the driving force a flow is produced.

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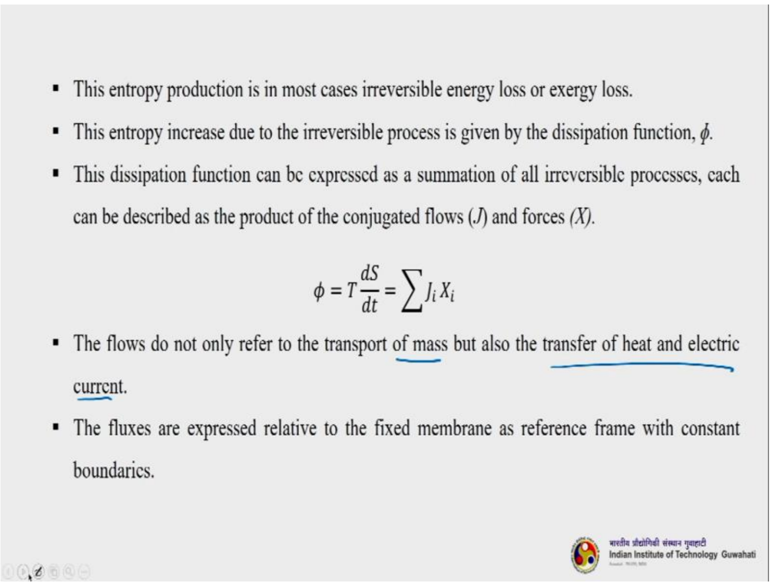

- This entropy production is in most cases irreversible energy loss or exergy loss.
- This entropy increase due to the irreversible process is given by the dissipation function, ϕ.
- This dissipation function can be expressed as a summation of all irreversible processes, each can be described as the product of the conjugated flows (*J*) and forces *(X)*.

$$\phi = T\frac{dS}{dt} = \sum J_i X_i$$

- The flows do not only refer to the transport of mass but also the transfer of heat and electric current.
- The fluxes are expressed relative to the fixed membrane as reference frame with constant boundaries.

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Now, this entropy production in most cases irreversible energy loss or energy loss. This entropy increase due to irreversible process is given by the dissipation function fi. This dissipation function can be expressed as a summation of all irreversible processes. So, each can be described as the product of the conjugated flows J and forces X. So, fi = T ds / dt. S is the entropy submission of J i X i.

So, J i is the flux and X i is the force. Now, the flows do not really only refer to the transport of mass but also transfer of heat and electrical current. This is also very important. So, the fluxes are expressed in relative to the fixed membrane as reference frame with constant boundaries.

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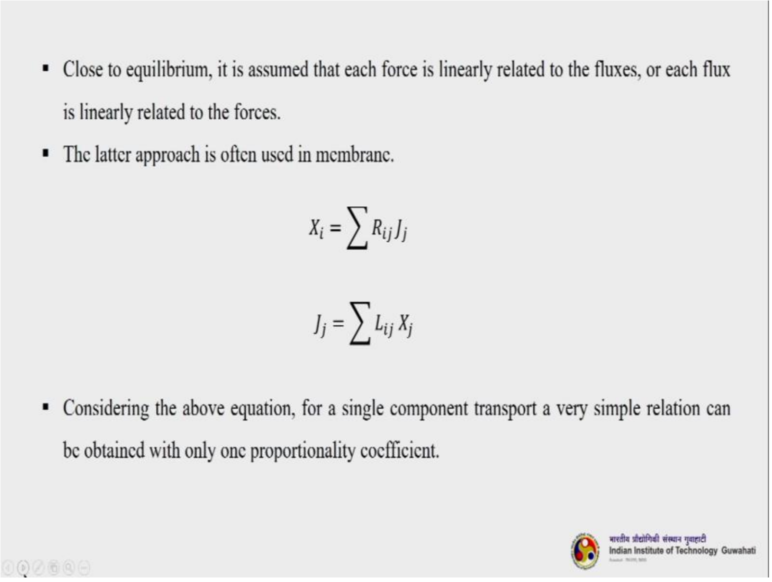

- Close to equilibrium, it is assumed that each force is linearly related to the fluxes, or each flux is linearly related to the forces.
- The latter approach is often used in membrane.

$$X_i = \sum R_{ij} J_j$$

$$J_j = \sum L_{ij} X_j$$

- Considering the above equation, for a single component transport a very simple relation can be obtained with only one proportionality coefficient.

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Close to equilibrium it is a assumed that each force is linearly related to the fluxes or each flux is linearly related to the forces. So, the latter approach is usually often used in membranes the force approximation. So, X i equals to summation of R ij and J j. J j can be written as summation of L ij X j. So, considering the above equation for a single component transport a very simple relationship can be obtained with only one proportionality coefficient. So, to idea is to make the life easier. So, that will use only one proportionality constant to derive the single component transport equation.

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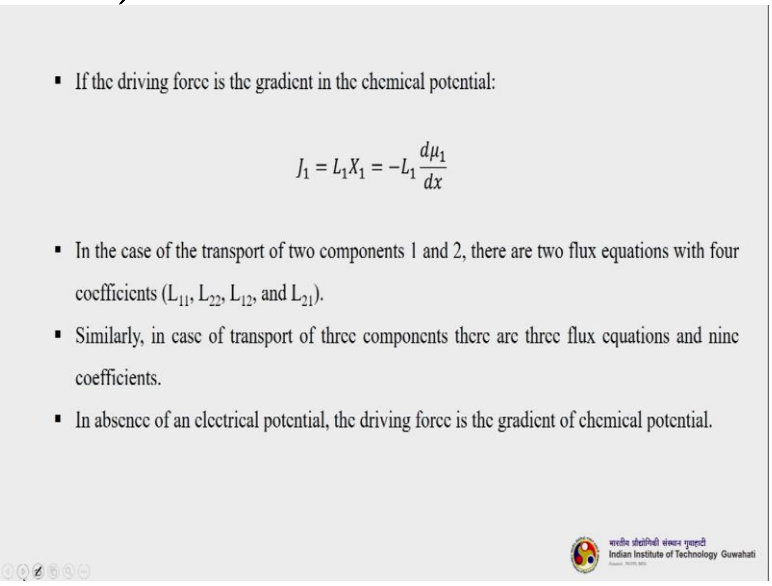

- If the driving force is the gradient in the chemical potential:

$$J_1 = L_1 X_1 = -L_1 \frac{d\mu_1}{dx}$$

- In the case of the transport of two components 1 and 2, there are two flux equations with four coefficients (L_{11}, L_{22}, L_{12}, and L_{21}).
- Similarly, in case of transport of three components there are three flux equations and nine coefficients.
- In absence of an electrical potential, the driving force is the gradient of chemical potential.

If the driving force is the gradient in the chemical potential, then we can write J 1 = L 1 X 1 = - L 1 d mu 1 by dx. Now, in case of the transport of 2 components that is 1 in 2 there are 2 flux equations with 4 coefficients. So, the same equation can be written and we can write in terms of different other components which can be expressed as L 1 1, L 2 2, L 1 2 and L 2 1. So, similarly, in case of transport of 3 components, there are 3 flux equations and 9 coefficients. So, in absence of an electrical potential the driving force is the gradient of chemical potential.

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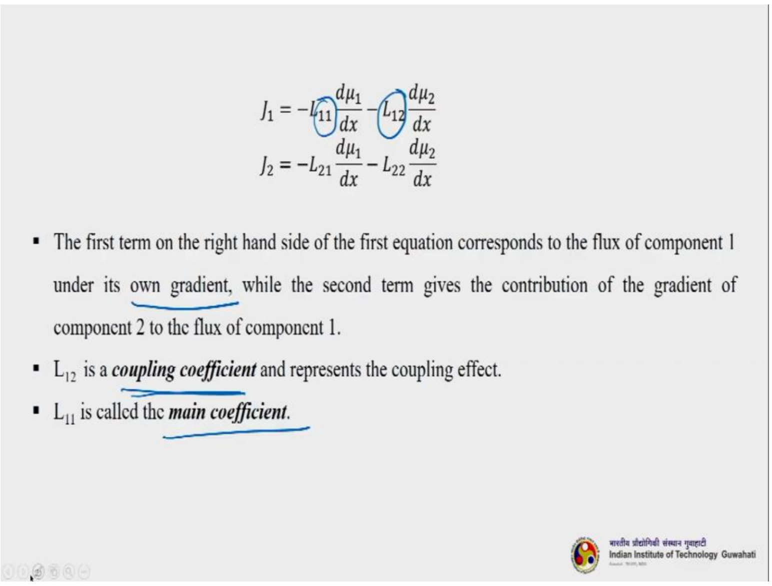

$$J_1 = -L_{11}\frac{d\mu_1}{dx} - L_{12}\frac{d\mu_2}{dx}$$

$$J_2 = -L_{21}\frac{d\mu_1}{dx} - L_{22}\frac{d\mu_2}{dx}$$

- The first term on the right hand side of the first equation corresponds to the flux of component 1 under its own gradient, while the second term gives the contribution of the gradient of component 2 to the flux of component 1.
- L_{12} is a ***coupling coefficient*** and represents the coupling effect.
- L_{11} is called the ***main coefficient***.

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So, how we can write this equation or just have a look at this 2 equations. J 1 = - L 1 1 d mu 1 / dx - L 1 2 d mu 2 / dx and J 2 = - L 2 1 d mu 1 by dx and - L 2 1 d mu 1 by dx. Now, what are those things now, the first term on the right hand side of the first equation corresponding to the flux of component 1 under its own gradient? While the second term gives the contribution of the gradient of the component 2 that of the flux of the component 1.

So, this is with own gradient and this is due to the contribution of component 2 the flux of component 1. That means, this one component 2 is also affecting the flux of component 1 and how it is affecting that can be expressed using that particular equation. So, that is why here L 1 2 is called a coupling coefficient and represents the coupling effect. How another component is affecting the transport one separate or one other component that is being expressed is coupling effects or we call this coefficient or coupling coefficient.

Whereas, the L 1 1 which is actually the flux of component 1 under its own gradient, so, that is why it is called L 1 1 is called the main coefficient.

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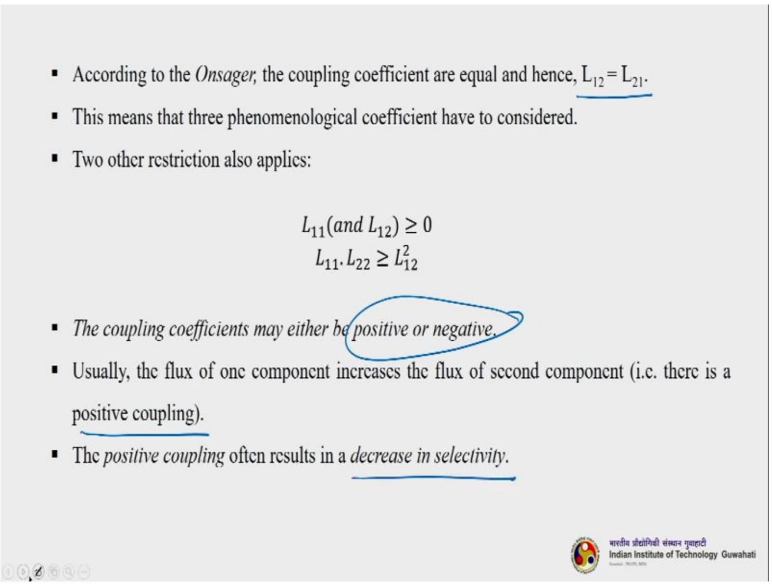

- According to the *Onsager*, the coupling coefficient are equal and hence, $L_{12} = L_{21}$.
- This means that three phenomenological coefficient have to considered.
- Two other restriction also applies:

$$L_{11}(and\ L_{12}) \geq 0$$
$$L_{11}.L_{22} \geq L_{12}^2$$

- *The coupling coefficients may either be positive or negative.*
- Usually, the flux of one component increases the flux of second component (i.e. there is a positive coupling).
- The *positive coupling* often results in a *decrease in selectivity*.

So, according to Onsager, the scientist who is actually proposed this nonlinear non equilibrium thermodynamics and this coupling coefficient. So, he says that coupling coefficients are equal hence we can write that L 1 2 = L 2 1. So this means that 3 phenomenological coefficients have to be considered. So we just reduced instead of 2 3. So, other restrictions also apply. So, these are the things which he is actually suggested.

L 1 1 and L 1 2 also should be > = 0, then the multiplication of L 1 1 and L 2 2 should be > = the square of the L 1 2. Now, the coupling coefficient may either be positive or negative. This is also very important. So, usually the flux of one component increases the flux of the second component. So, when the flux of one component is getting increased by the effect of or contribution from the flux of another component then this is called positive component coupling. The positive coupling often results and decrease in selectivity which is not good actually.

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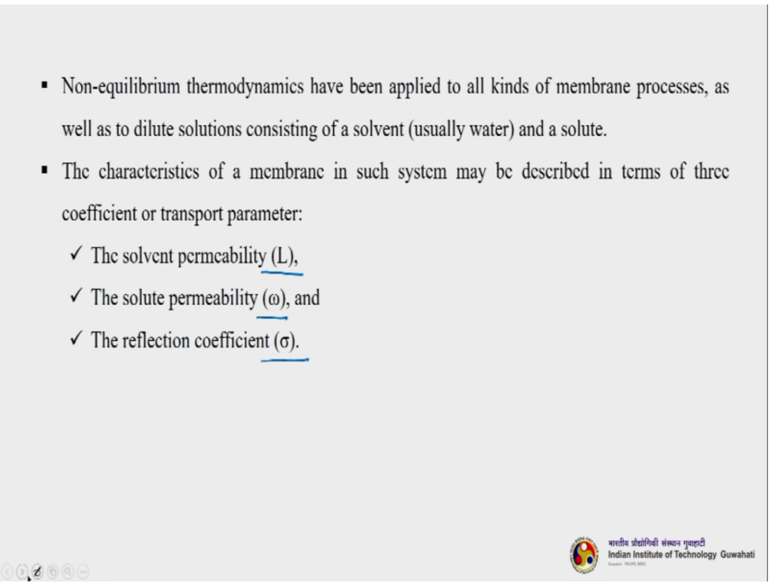

- Non-equilibrium thermodynamics have been applied to all kinds of membrane processes, as well as to dilute solutions consisting of a solvent (usually water) and a solute.
- The characteristics of a membrane in such system may be described in terms of three coefficient or transport parameter:
  - ✓ The solvent permeability $\underline{(L)}$,
  - ✓ The solute permeability $\underline{(\omega)}$, and
  - ✓ The reflection coefficient $\underline{(\sigma)}$.

So, non-equilibrium thermodynamics have been applied to all kinds of membrane processes as well as to dilute solutions consisting of a solvent which is actually usually water and solute. The characteristics of a membrane in such a system may be described in terms of 3 coefficient or transport parameters. So, what are those the first one is the solvent permeability which is given by L. The second is solute permeability which is given by this omega and the third is reflection coefficient which is given by this sigma.

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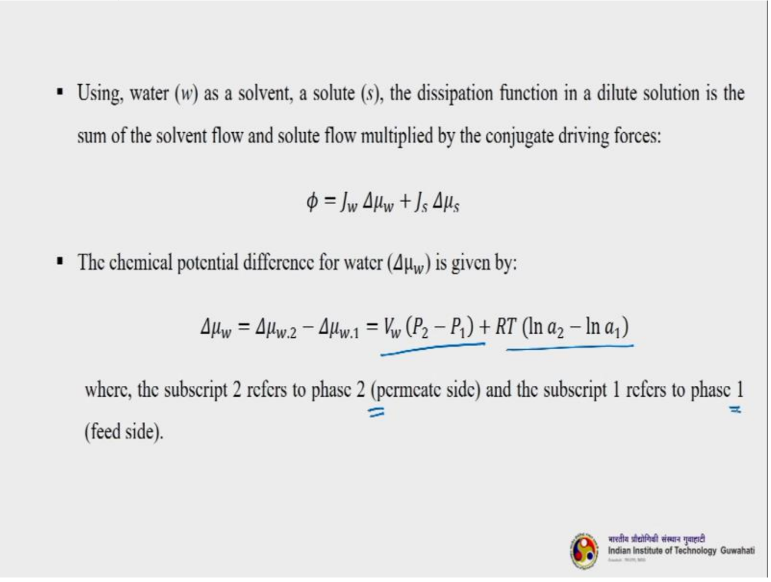

- Using, water (w) as a solvent, a solute (s), the dissipation function in a dilute solution is the sum of the solvent flow and solute flow multiplied by the conjugate driving forces:

$$\phi = J_w \, \Delta\mu_w + J_s \, \Delta\mu_s$$

- The chemical potential difference for water ($\Delta\mu_w$) is given by:

$$\Delta\mu_w = \Delta\mu_{w.2} - \Delta\mu_{w.1} = \underline{V_w (P_2 - P_1)} + RT \, \underline{(\ln a_2 - \ln a_1)}$$

where, the subscript 2 refers to phase 2 (permeate side) and the subscript 1 refers to phase 1 (feed side).

Using water is a solvent and a solute X the dissipation function in a dilute solution is the sum of the solvent flow and solute flow multiplied by the conjugate driving forces. So, you can write the dissipation function phi is a mixture of we can say the summation of 2 different fluxes that one is J W which is the flux due to water another is the J s which is the flux due to salt. So you can write dissipation function phi = j w and then delta mu w + J S delta mu S.

Now the chemical potential difference for water is given by so delta mu 2 - delta mu 1 which is we can write in terms of pressure is like this V w that is the molar volume p 2 - p 1 + RT ln a 2 - ln a 1. So, where subscript 2 refers to the phase 2 permeate side and subscript 1 refers to the phase 1 that is feed side.

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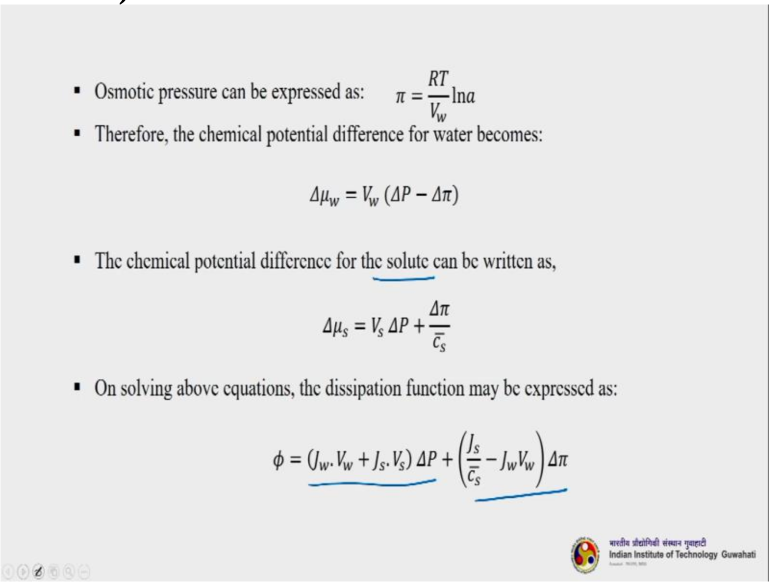

- Osmotic pressure can be expressed as: $\pi = \frac{RT}{V_w} \ln a$
- Therefore, the chemical potential difference for water becomes:

$$\Delta\mu_w = V_w\,(\Delta P - \Delta\pi)$$

- The chemical potential difference for the solute can be written as,

$$\Delta\mu_s = V_s\,\Delta P + \frac{\Delta\pi}{\bar{c}_s}$$

- On solving above equations, the dissipation function may be expressed as:

$$\phi = \underline{(J_w.V_w + J_s.V_s)}\,\Delta P + \left(\frac{J_s}{\bar{c}_s} - \underline{J_w V_w}\right)\Delta\pi$$

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Osmotic pressure we can express pi – RT / V W ln a. So, therefore, the chemical potential difference of the water becomes delta mu w = V w delta P - delta pi writing expressing in terms of osmotic pressure. So, the chemical potential difference for the solute can be written as V s delta P + delta pi by C s that is the concentration of the solid. So, on solving the above equation that dissipation function some dissipation may be expressed is as , J w V w + J s V s into delta P. So, this is the pressure term then J s / C s – J w V w into delta pi. This is due to the osmotic pressure.

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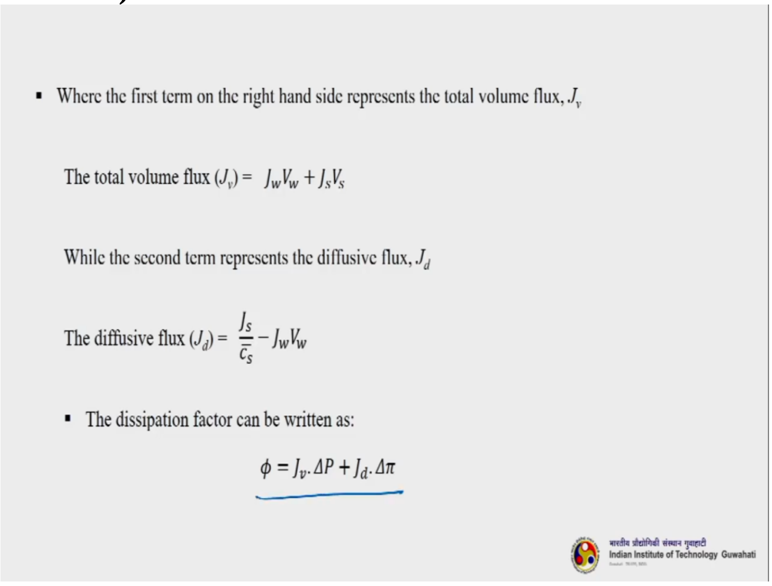

- Where the first term on the right hand side represents the total volume flux, J_v

The total volume flux (J_v) = $J_w V_w + J_s V_s$

While the second term represents the diffusive flux, J_d

The diffusive flux (J_d) = $\frac{J_s}{\bar{c}_s} - J_w V_w$

- The dissipation factor can be written as:

$$\underline{\phi = J_v.\Delta P + J_d.\Delta\pi}$$

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The first term represents the total volume plus J v. So total volume flux J v = J w V w + J s V s. While the second term represents that diffusive flux that is J d. So, the diffusive flux is J s / C s - J w V w. Now, the dissipation factor has this can be written in terms of the total volume flux as well as total and that diffusive flux phi = J v delta P + J d delta pi.

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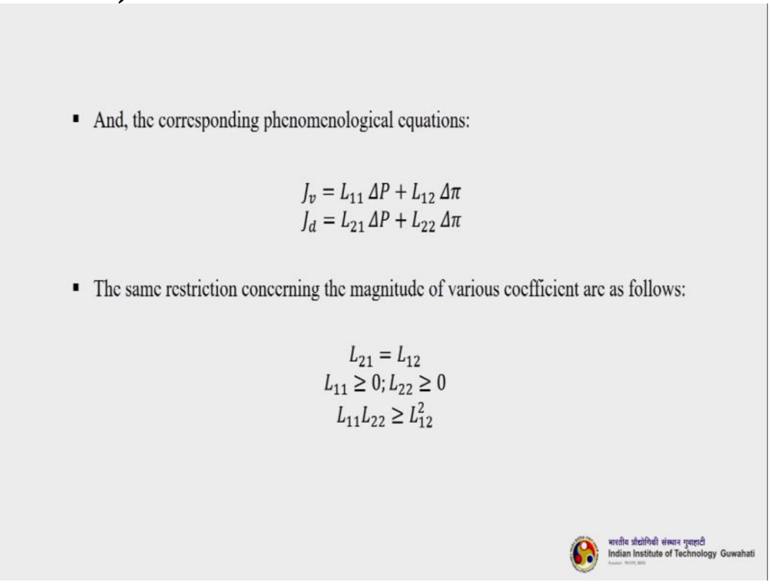

- And, the corresponding phenomenological equations:

$$J_v = L_{11}\, \Delta P + L_{12}\, \Delta\pi$$
$$J_d = L_{21}\, \Delta P + L_{22}\, \Delta\pi$$

- The same restriction concerning the magnitude of various coefficient are as follows:

$$L_{21} = L_{12}$$
$$L_{11} \geq 0; L_{22} \geq 0$$
$$L_{11}L_{22} \geq L_{12}^2$$

So, the corresponding phenomenological equations will be J v = L 1 1 l delta P + L 1 2 delta pi and J d = L 2 1 delta P + L 2 2 delta pi. Now, again the same restrictions which was recommended by Onsager also applies here concerning the of course, the magnitude of various coefficients. So L 2 1 = L 1 2 and L 1 1 should be > = 0. L 2 2 should also be > = 0 and the multiplication of the factor this L 11 and L 2 2 must be > = L l 1 L 2 2.

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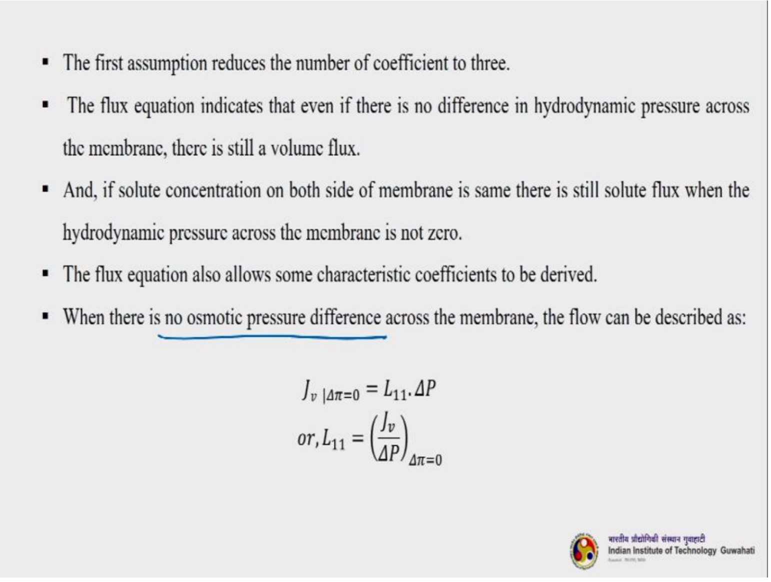

- The first assumption reduces the number of coefficient to three.
- The flux equation indicates that even if there is no difference in hydrodynamic pressure across the membrane, there is still a volume flux.
- And, if solute concentration on both side of membrane is same there is still solute flux when the hydrodynamic pressure across the membrane is not zero.
- The flux equation also allows some characteristic coefficients to be derived.
- When there is no osmotic pressure difference across the membrane, the flow can be described as:

$$J_v\,|_{\Delta\pi=0} = L_{11}.\Delta P$$
$$or, L_{11} = \left(\frac{J_v}{\Delta P}\right)_{\Delta\pi=0}$$

The first assumption reduces the number of coefficient to 3. The flux question indicates that even if there is no difference in hydrodynamic pressure across the membrane, there is still a volume flux. This is very important to understand. So, if there is no hydrodynamic pressure difference across the membrane still there should be a flux. And if solute concentration on both sides of the membrane is same, there is still solute flux when the hydrodynamic pressure across the membrane is not 0.

So, the flux equation also allow some characteristic coefficients to be derived when there is no Osmotic pressure difference across the membrane. So, when there is Osmotic pressure difference across the membrane the flow can be described as this So, that means, when Osmotic pressure difference means delta pi = 0. So, the total volume flux when delta pi = L 1 1 delta P or we can write L 1 1 = J v / delta P when delta pi becomes 0.

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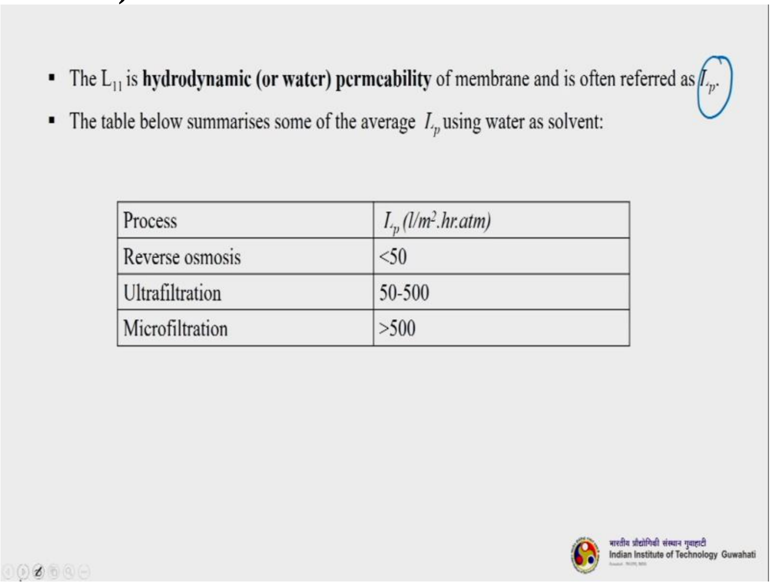

- The L_{11} is **hydrodynamic (or water) permeability** of membrane and is often referred as L_p.
- The table below summarises some of the average L_p using water as solvent:

Process	L_p ($l/m^2.hr.atm$)
Reverse osmosis	<50
Ultrafiltration	50-500
Microfiltration	>500

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So, L 11 is the hydrodynamic or water permeability of the membrane and is often referred to as L P. So, please do not confuse with different types of notation in different books. So, L 1 1 is the hydrogen record water permeability, which is also called as the L p known as also L p. So the table summarizes some of the average L p using water is solvent for reverse osmosis it is < 50 ultrafiltration 50 to 500 microfiltration > 500. So the unit is litre per meter square hour atmosphere.

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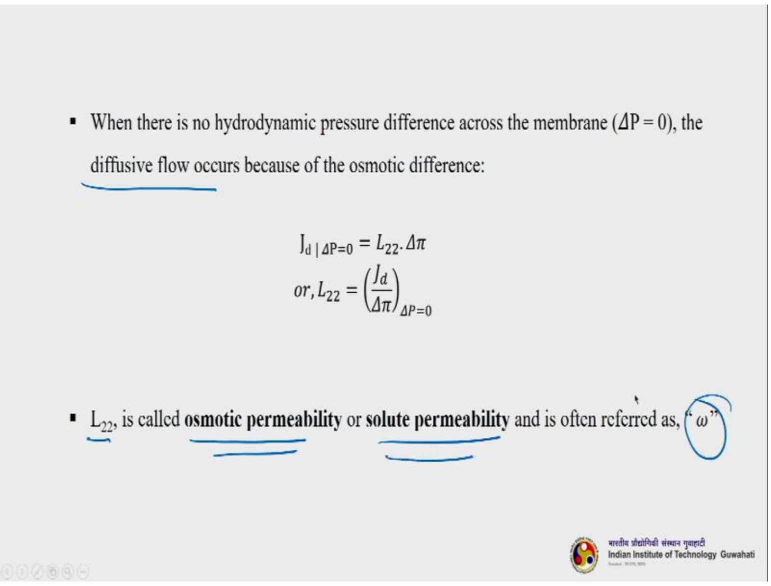

- When there is no hydrodynamic pressure difference across the membrane ($\Delta P = 0$), the diffusive flow occurs because of the osmotic difference:

$$J_d|_{\Delta P=0} = L_{22}.\Delta\pi$$

$$or, L_{22} = \left(\frac{J_d}{\Delta\pi}\right)_{\Delta P=0}$$

- L_{22}, is called **osmotic permeability** or **solute permeability** and is often referred as, "ω"

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So when there is no hydrodynamic pressure difference across the membrane that means delta P = 0, the diffusive flow occurs because of the osmotic difference. So J d at delta P = 0 = delta L 2 2 delta pi, or we can write L 2 2 = J d by delta pi, when delta P = 0. So, what is L 2 2? L 2 2 is called the osmotic permeability or solute permeability and is often referred as omega.

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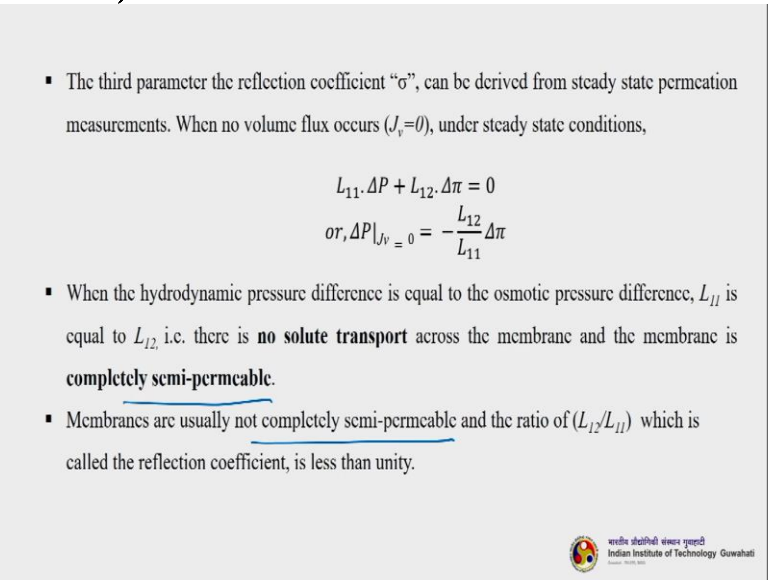

- The third parameter the reflection coefficient "σ", can be derived from steady state permeation measurements. When no volume flux occurs ($J_v=0$), under steady state conditions,

$$L_{11}.\Delta P + L_{12}.\Delta\pi = 0$$

$$or, \Delta P|_{J_v=0} = -\frac{L_{12}}{L_{11}}\Delta\pi$$

- When the hydrodynamic pressure difference is equal to the osmotic pressure difference, L_{11} is equal to L_{12}, i.e. there is **no solute transport** across the membrane and the membrane is **completely semi-permeable**.
- Membranes are usually not completely semi-permeable and the ratio of (L_{12}/L_{11}) which is called the reflection coefficient, is less than unity.

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The third parameter, the reflection coefficient can be derived from the steady state permission measurements when no volume flux occurs, that means, J P = 0 under steady state conditions. L 1 l delta P + L 1 2 delta pi = 0, that means delta P when J P = 0 we can write that it is = - L 1 2 / L 1 1 delta pi. Now, when the hydrodynamic pressure difference is equal to the osmotic pressure difference, L 1 1 = L 1 2.

And there is no solute transport across the membrane and the membrane is completely semi permeable. This is what ideally a membrane should be. However membranes are actually in real life practices, they are not completely semi permeable. And the ratio of L 1 2 / L 1 1 which is called the reflection coefficient is usually less than unity.

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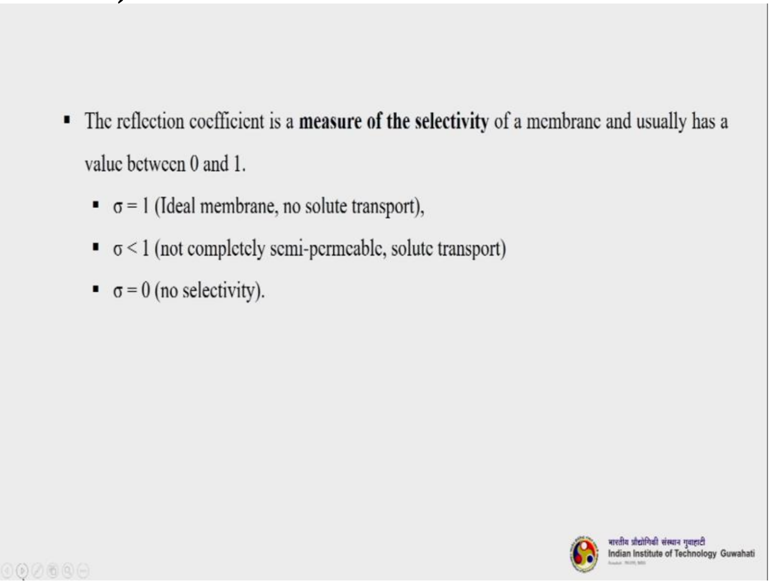

- The reflection coefficient is a **measure of the selectivity** of a membrane and usually has a value between 0 and 1.
  - $\sigma = 1$ (Ideal membrane, no solute transport),
  - $\sigma < 1$ (not completely semi-permeable, solute transport)
  - $\sigma = 0$ (no selectivity).

So, the reflection coefficient is a measure of the selectivity of the membrane and usually has a value between 0 to 1. So if it is one, so it is ideal membrane that means no solute transport, if it is less than one not completely semi permeable. So solute transport occurs, if it is 0, so there is no selectivity. So this reflection coefficient is a very important parameter which is directly tells us that selectivity of the membrane.

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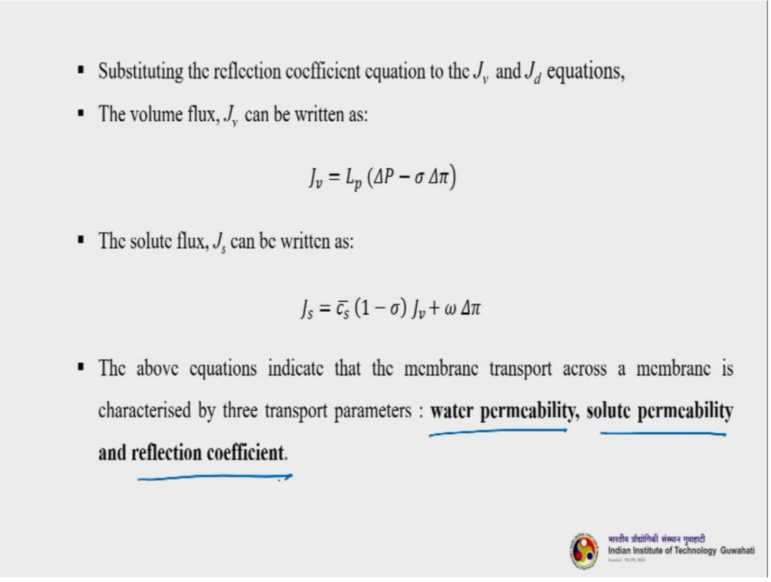

- Substituting the reflection coefficient equation to the J_v and J_d equations,
- The volume flux, J_v can be written as:

$$J_v = L_p\,(\Delta P - \sigma\,\Delta\pi)$$

- The solute flux, J_s can be written as:

$$J_s = \bar{c}_s\,(1 - \sigma)\,J_v + \omega\,\Delta\pi$$

- The above equations indicate that the membrane transport across a membrane is characterised by three transport parameters : **water permeability, solute permeability and reflection coefficient.**

So, if you substitute this reflection coefficient equation to the, this volume flux and the diffusive flux equation, then we can write volume flux is volume plus J P = L p delta P minus the sigma delta pi. So, solute flux also can be written as J s = c s 1 - sigma J v omega + omega into delta pi. Now, the above equations indicate that the membrane transport across the membrane is characterized by 3 transport parameters. So, what are those, first one water permeability, second solid permeability and third is reflection coefficient.

So, let us now summarize that the membrane transport is governed by these 3 things, first is water permeability, secondly solute permeability and third is the reflection coefficient.

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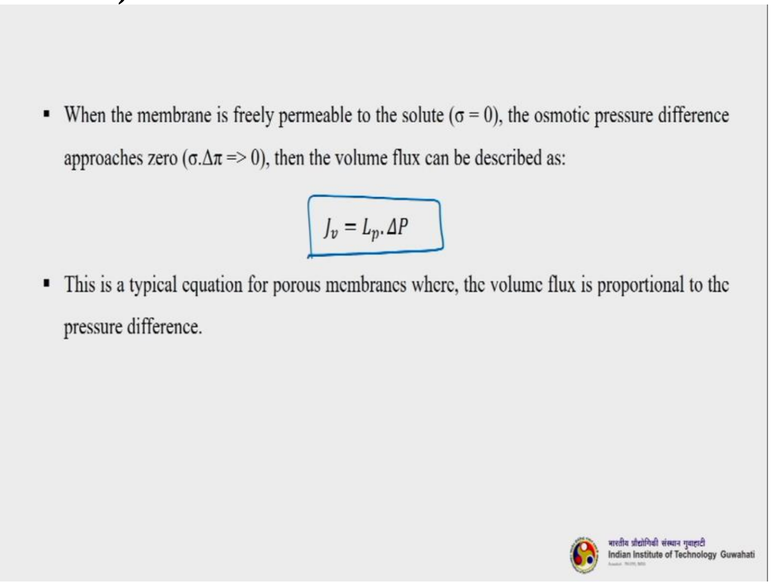

- When the membrane is freely permeable to the solute ($\sigma = 0$), the osmotic pressure difference approaches zero ($\sigma.\Delta\pi \Rightarrow 0$), then the volume flux can be described as:

$$\boxed{J_v = L_p.\Delta P}$$

- This is a typical equation for porous membranes where, the volume flux is proportional to the pressure difference.

So, when membrane is freely permeable to the solute, so, that is you see sigma = 0, the osmotic pressure difference approaches 0. Then the volume flux can be written as J v = delta L p delta P. So, this is the typical equation for porous membrane. These are transport equation right where the volume flux is proportional to the pressure difference. So, you can see this your volume flux is directly related to the pressure difference or an LP usually the LP is the constant.

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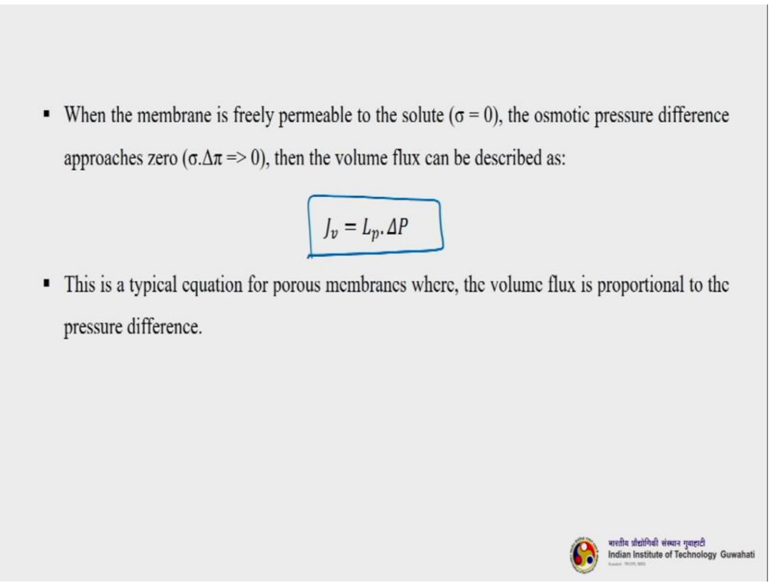

- When the membrane is freely permeable to the solute ($\sigma = 0$), the osmotic pressure difference approaches zero ($\sigma.\Delta\pi \Rightarrow 0$), then the volume flux can be described as:

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The thermodynamics of irreversible processes are very useful for understanding and quantifying the coupling phenomena. However structure related membrane models are more useful than the reversible thermodynamic approach for developing specific membranes. Transport occurs through the pore in porous membrane rather than the dense matrix and the structure parameters such as pore size, pore size distribution, porosity and pore dimensions are important.

The selectivity of such membranes is based mainly on differences between particles and pore size. Because of the existence of a diving force the component within the membrane is transported from one side to another by diffusion.

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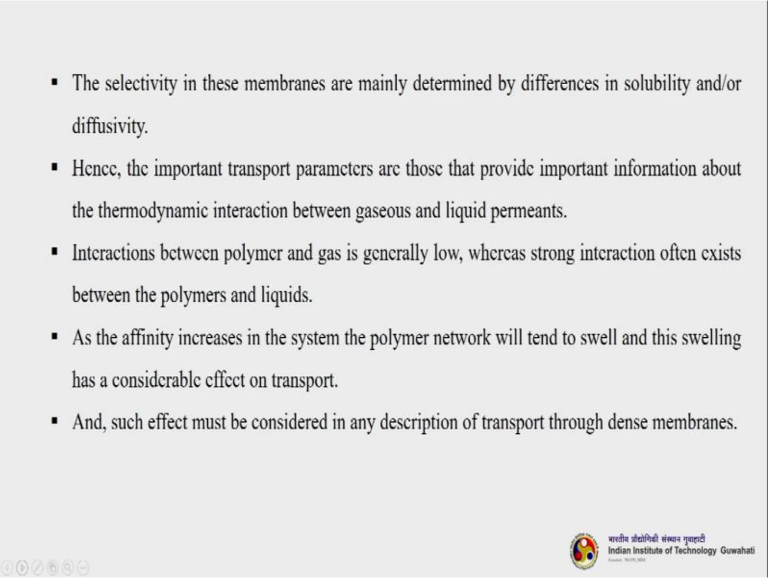

- The selectivity in these membranes are mainly determined by differences in solubility and/or diffusivity.
- Hence, the important transport parameters are those that provide important information about the thermodynamic interaction between gaseous and liquid permeants.
- Interactions between polymer and gas is generally low, whereas strong interaction often exists between the polymers and liquids.
- As the affinity increases in the system the polymer network will tend to swell and this swelling has a considerable effect on transport.
- And, such effect must be considered in any description of transport through dense membranes.

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The selectivity in these membranes are mainly determined by differences in solubility and/or diffusivity Hence, the important transport parameters are those that provide important information about the thermodynamic interaction between gaseous and liquid permeants. Interactions between polymer and gases is generally low, whereas strong interaction upon exist between the polymer and the liquids. As the affinity increases in the system the polymer network will tend to swell and this swelling has a considerable effect on transport.

And such effect must be considered in any description of transport through the dense membranes. So, that is the problem in dense membranes. So, these are some of the actually problems when you dilute dense membranes. So, more or less in industrial practices on industrial parlance, most of the membranes that are being used in commercial or in large scale are all porous membranes. That use of non-porous membrane are very very less though it is being used commercially as well as industrially also.

However, due to these transport problems, and there are other problems necessarily the dense membrane. So usually porous membrane serving people.

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Text/References

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- K. Nath, Membrane Separation Processes, PHI, 2008.
- M. Cheryan, Ultrafiltration & Microfiltration Handbook, Technomic, 1998.
- Richard W. Baker, Membrane Technology and Applications, Wiley, 2012.

So, you can see the book Mulder for today's lecture actually mostly it is taken from that. And apart from today's lecture, you can also refer the last book, Richard Baker. In here also transport is also given very nicely.

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Module	Module name	Lecture	Title of lecture
05	Porous and non-porous membrane transport and osmosis concept	13	• Transport through porous membranes • Transport of gases • Knudsen flow • Friction model

Thank you

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

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So the next class, we are discussing the transport of porous and non-porous membranes, and then we will discuss also the concept of osmosis. So we will discuss transport through porous membrane, transport of gases, knudsen flow and friction model in our next lecture. So thank you very much. In case you have any query do feel free to write to me at kmohanty@iitg.ac.in. Thank you.